Synthesis and characterization of polymacromonomers based on polyethers

DISSERTATION

Zur Erlangung des akademischen Grades

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von
DC Aleksandra Mendrek

geboren am 24. Januar 1977 in Sosnowiec, Polen

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Submitted to

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To my beloved husband Sebastian

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1. General introduction

A particularly challenging aspect of polymer synthesis concerns the development of techniques for the preparation of macromolecular materials with well-defined structures. An essential requirement for many applications is the precise control of copolymer structure in terms of composition, molecular weight, molecular weight distribution (dispersity index), or balance between hydrophilic and hydrophobic segments. Additionally, it is well known that solution and bulk properties of a polymer are drastically influenced by its architecture and differ significantly for linear and non-linear structures with similar molecular weight.

Recently the branched and star-like polymers have attached attention due to their unique properties [1-5]. Their solutions show lower viscosity in comparison to their linear counterparts. Additionally, their properties may be influenced by the proper modification of end groups, which number is much higher in a branched molecule then in the linear chain. The properties in condensed phase are also different as the chain entanglements, which decide about the viscoelastic properties of the materials, are not likely to be formed.

Among the branched polymers a special class are regularly branched copolymer brushes. Depending on the relative length of the branch versus the polymer backbone such polymers take a conformation that looks like a star or a brush. Generally, there are three methods which were applied to synthesize cylindrical polymer brushes: "*grafting onto*", "*grafting from*" and "*grafting through*".

In the "*grafting onto*" technique [6-8], schematically presented in Figure 1.1, the polymer backbone and the side chains are synthesized separately and can be well characterized (the molecular weights can be found for example by size exclusion chromatography (*SEC*)). As next preformed polymers, having reactive chain ends, react and attach to a backbone main chain which bears functional groups. This results in branched polymer formation. The advantage of this method is that both the main chain and side chain length or molecular weight distribution can be influenced (controlled methods of polymers synthesis). However, in general only a small, insufficient amount of polymer reacts with the backbone resulting in the low grafting density. The limitation of such grafting method results from the fact that the crowding of the chains, which have already reacted with the backbone, hinders the diffusion of new chain ends to the polymer backbone. As the result the position of branches is random and their number broadly distributed. Additionally, as the incomplete conversion of side

chains is observed their removal form the reaction mixture is necessary, what in most cases is complicated.

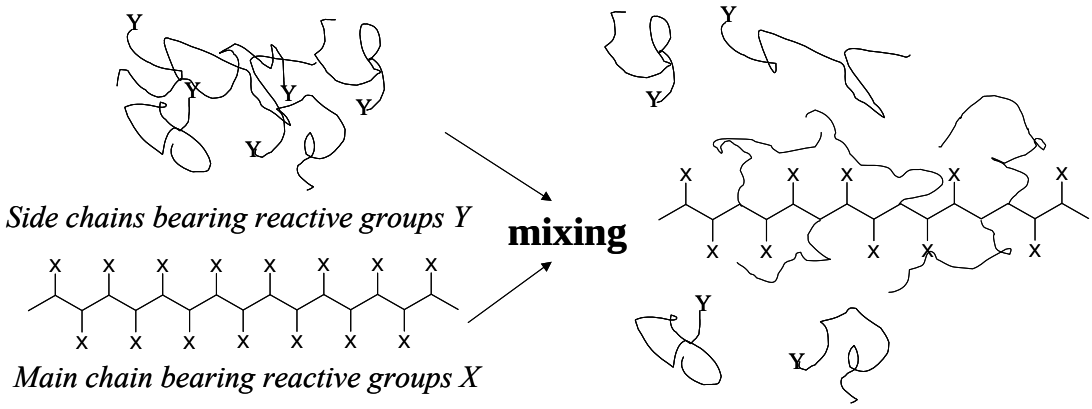


Figure 1.1. "*Grafting onto*" technique.

The "*grafting from*" technique is based on the preparation of branched polymers by grafting of the side chains directly from the main polymer chain [9-11], what is presented in Figure 1.2. The polymer backbone possess pendant groups able to initiate the polymerisation of monomer, used for the side chains preparation. In order to obtain well-defined side chains a commonly used polymerisation technique is *ATRP*, although other techniques like anionic polymerisation were also applied [12]. By this method the well-defined polymer brushes with high and uniform grafting density can be obtained. However, only the backbone can be characterized directly. The molecular weight of the side chains can only be calculated indirectly from the overall molecular weight of the brush, or if possible, by subsequent detachment of the side chains from the backbone (for example by hydrolysing the ester linkage in the brushes). However, the purification of resulting polymer is simpler comparing to the previous method. The unreacted monomer can be removed for example by precipitation as its properties are different from the properties of obtained brush.

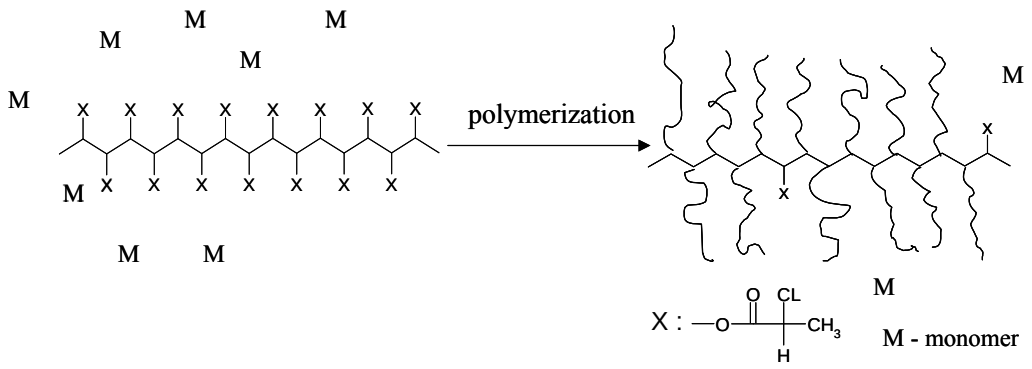


Figure 1.2. "*Grafting from*" technique.

The "*grafting through*" synthesis of branched polymer presented in Figure 1.3 is based on homopolymerisation of macromonomers bearing the polymerizable group [13-15] (i.e. vinyl group) and will be the topic of this dissertation. This is the good route to regular, multibranched polymers with very high branch density. Generally, the length of branches and backbone in a comb polymer can be controlled during the synthesis. An advantage here is the use of a known macromonomer as a branch, where the molecular weight and its distribution is predicted and controlled by the method of preparation (i.e. living anionic or cationic polymerisation, group transfer polymerisation, *ATRP*) [15-17]. Also the backbone length and its distribution can be in principle similarly controlled by the method of preparation. However, on this field only few studies have been completed successfully [18-19].

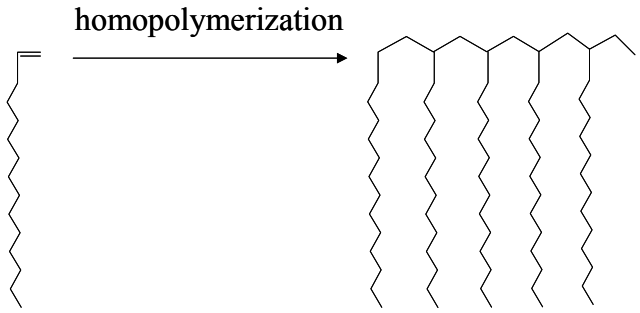


Figure 1.3. "*Grafting through*" technique

The main disadvantage of the "*grafting through*" method is that the macromonomers often polymerise with difficulties because of their high molecular weight as compared to lower molecular weight monomers [20]. High segment density around the propagating site is considered to prevent the propagating active site from approaching polymerizable end group of macromonomers via the steric effect. As the result the degree of polymerisation of polymacromonomers is usually low.

2. Objectives

It was found that the feature which has great influence on both the rate of the polymerisation of macromonomers and degree of polymerisation of the polymacromonomers is self organization of macromonomers in the solvent. Such behaviour was observed in case of amphiphilic macromonomers, for example polyethylene oxide macromonomers, where the polymerisation in water is very fast and the obtained degree of polymerisation high [21-24]. This has given a new impetus to the studies of the synthesis of the brush molecules of well-defined structure by "*grafting through*" method.

The aim of this work was the synthesis of hydrophilic macromonomers of glycidol (2,3-epoxypropanol) terminated with vinyl benzyl groups as well as of amphiphilic block macromonomers of glycidol and phenyl glycidyl ether terminated with vinyl benzyl group and their polymerisation. The work will be divided into three parts. In the first part the preparation of new macromonomers based on poly(glycidol) and their characterization using a variety of available techniques will be described. In the second part the application of synthesised macromonomers for the synthesis of branched polymers (polymacromonomers) and their characterization will be presented. Finally, the formation of temperature sensitive brushes will be shown.

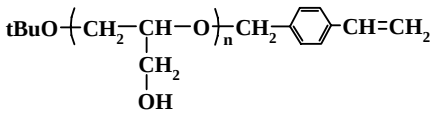
In order to achieve the desired goal the following procedures will be applied:

- As preparation method controlled anionic polymerisation of oxiranes will be applied. However, it is commonly known that direct polymerisation of glycidol leads to branched structures [25-27]. Thus, as the synthesis of linear poly(glycidol) macromonomers is desired, the hydroxyl group of glycidol will be reversibly protected using the method presented by Spassky *et al.* [28]. As the polymerisation of such protected monomer was already applied in our group [29-32] it is expected that the good control of both molecular weight and M_w/M_n of poly(glycidol) will be obtained.

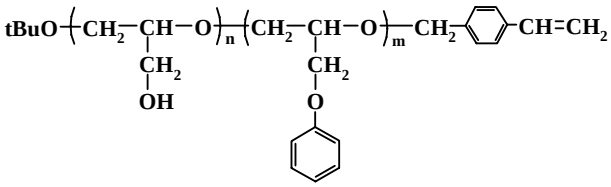
- Reactive vinyl benzyl groups will be introduced to the main chain of the polymer by the termination of living macroanion (obtained after polymerisation) with *p*-vinylbenzyl styrene chloride. Such procedure was already used in our group and macromonomer presented in Scheme 2.1.a was already obtained [32].

- The synthesis of amphiphilic block macromonomers was not described in the literature before and will be carried out by the sequential monomer addition and. As the hydrophobic spacer a short block of poly(phenyl glycidyl ether) was chosen. The proper order of addition of protected glycidol and phenyl glycidyl ether should yield the different architectures of macromonomers. The spacer will be placed at reactive vinyl benzyl group or at the opposite end of macromonomer (see Scheme 2.1.b, c). It is expected that the introduction of the second monomer to the polymerisation system of protected glycidol will not cause the perturbation in the system and the synthesis of well-defined macromonomers presented in Scheme 2.1. will be possible.

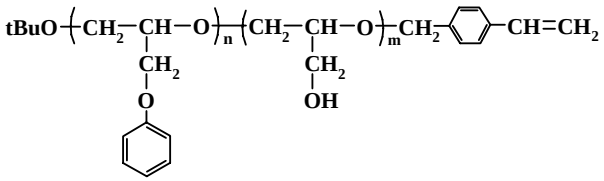
a) *α-t*–butoxy-*ω*-vinylbenzyl-poly(glycidol)



b) *α-t*–butoxy-*ω*-vinylbenzyl- poly(glycidol)-*b*-poly(phenyl glycidyl ether)



c) *α-t*-butoxy-*ω*-vinylbenzyl-poly(phenyl glycidyl ether)-*b*-poly(glycidol)



Scheme 2.1. Targeted macromonomers structure.

- The aggregation behaviour of all synthesised macromonomers in water will be investigated. It is expected that, similarly to poly(ethylene oxide) macromonomers [21-24], synthesised amphiphilic chains will form micellar structures in that solvent, what is very important taking into consideration the polymerisation behaviour of macromonomers and will be discussed in details in the next chapters.

- The macromonomers will be polymerised using two different polymerisation techniques – conventional radical and controlled radical (*ATRP*) polymerisation in different solvents (water, tetrahydrofuran, dimethyl formamide). In conventional radical technique two initiators will be used – *4,4'*-azobis (*4*-cyanovaleric acid) (*AVA*) and *2,2'*-azobis(isobutyronitrile) (*AIBN*), but in case of *ATRP* the reaction conditions have to be found. Also *ATRP* of

macromonomers initiated by the *ATRP* moiety attached to the surface will be performed. Once the micellization or any aggregation in water will be observed the high rate of the reaction as well as high degree of polymerisations are expected. Additionally, the use of the controlled polymerisation methods should result in the control of the degree of polymerisation and narrow polydispersity indexes of polymacromonomers. The obtained compounds will be characterized using such analytical method as ^{1}H *NMR, SEC* and *AFM*. Finally, the modification of hydroxyl groups of poly(glycidol) will be carried out in order to obtain temperature sensitive brushes.

3. Literature review

3.1. Definition of macromonomer

A macromonomer is a reactive oligomer or polymer with the molecular weight usually not exceeding 10^3 – 10^4 g/mol. A polymerizable functional group is connected to a chain end. A pioneering work on the synthesis of polymers having a polymerizable group is dated back to 1958. However, the work was not fully recognized as a useful technique to prepare graft copolymers until Milkovich, who as first obtained *ω*-vinylbenzyl-poly(styrene) macromonomer presented in Figure 3.1. [33-35].

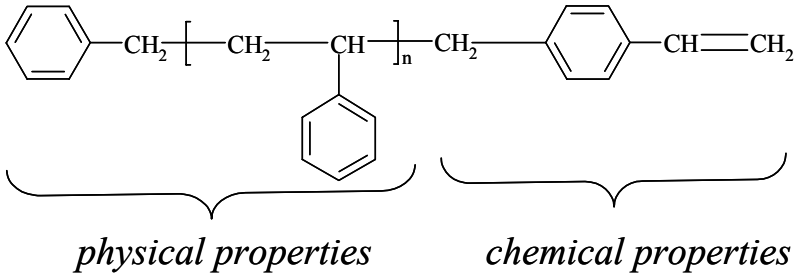


Figure 3.1. An example of the chemical structure of a macromonomer [33-35].

Generally, macromonomers can be considered molecules that consist of two parts; one part, called *tail*, is a polymer chain influencing the physical properties of the structure, and the other part, called *head*, is the end functional group influencing chemical reactivity for polymerisations reactions of macromonomer [20]. Change of the chemical structure of the polymer chain provides macromonomers with various properties and influences such parameters like solubility or glass temperature (T_g). The primary factor affecting the chemical reactivity in polymerisation processes is the type of macromonomer end group. The reactivity of macromonomers usually follows the reactivity of the low molecular weight monomer carrying the same functional group [36].

Recently, great attention was paid to the synthesis and application of amphiphilic macromonomers [21-24, 37]. Such macromonomers consist of the hydrophilic *tail* soluble for example in water and of hydrophobic *head* insoluble in the mentioned solvent. The use of such macromonomers seems to be of interest, due to their hydrophilic-hydrophobic character, they tend to form micellar or aggregate structures in selective solvents, what is very important in applications [21-24].

3.2. Synthesis of macromonomers – general synthetic methods

3.2.1. Introduction

In order to use the macromonomers in direction of synthesis of polymacromonomers with expected structure great care has to be given to the preparation of the macromonomers themselves. The methods that turn out to be best suited for the synthesis of well-defined macromonomers are those based on the living or controlled polymerisation. Among them anionic [38], cationic [39], coordinate-anionic [40] as well as radical polymerisations [41-43] (group transfer, atom transfer radical polymerisation) were successfully applied. However, in case of some monomers (vinylpyrrolidone, acrylamide, vinylchloride) the application of controlled polymerisation methods has not been reported and such techniques as radical polymerisations or step-growth processes are used in synthesis of macromonomers [44-46].

Taking into account the way of end group introduction into polymer chain macromonomers are usually synthesized in one of four methods described below[47] (equations from 3.1. to 3.6.). The choice of the method is connected with the type of polymerisation system, where such parameters as initiator, terminator, monomer or solvent have to be taken into account, before the chosen method will be applied.

a) *End-capping* (termination) of a living polymer using the compound carrying reactive group ($x - F$) [44].

$$P_n^* + x - F \longrightarrow P_n^* - F \qquad \textbf{(3.1.)}$$

The most commonly introduced group using the *end-capping* method is the double bond. However, that method can be only applied in the systems where no transfer reactions appear during termination of living polymer chain, which has to be still active after the conversion of the monomer. Additionally, in order to obtain fully functionalized macromonomers the termination reaction must proceed quantitatively.

b) Initiation of living polymerisation by the compound carrying reactive group ($F - I$) [39].

$$F - I + nM \rightarrow F - I - P_n^* \rightarrow F - I - P_n \qquad \textbf{(3.2.)}$$

The application of this method requires fast initiation of polymerisation by the applied initiator, what limit this method only to controlled polymerisations systems. Moreover, the

polymerizable group of the initiator (*F*) has to be inert upon preparation of the macromonomer and do not react with any component of the polymerisation system. Additionally, no chain transfer reaction can proceed in the system.

c) Transformation of available end-functional group into desired one [44].

$$I + nM \rightarrow P_n - y \quad \textbf{(3.3.)}$$

$$P_n - y + x - F \rightarrow P_n - F \quad \textbf{(3.4.)}$$

This is the two step reaction, where the final macromonomer is obtained by transformation of one of the end groups of obtained polymer. However, it has to be taken into account that such transformation should proceed quantitatively.

d) Polyaddition.

$$F - P - x \rightarrow F - P_n - x \quad \textbf{(3.5.)}$$

$$F - P - F + x - Q - x \rightarrow F - [P\ Q]_n - x \quad \textbf{(3.6.)}$$

Polyaddition of bifunctional monomer (for example vinyl and silane groups (hydrosilylation)) or the reaction between two compounds with different functionality, where one is vinyl group leads to macromonomers directly [48].

Among the described methods the first two are simple and usually yield best-defined macromonomers of a controlled degree of polymerisation with a narrow molecular weight distribution, but depend of proper combination of living polymerisation with an effective terminator or initiator carrying a polymerising group or its protected form. The third method uses end-functionalized polymers such as those obtained from chain-transfer-controlled radical polymerisation and polycondensation. However, also polymers obtained by controlled polymerisation techniques are modified. The last very specific method of macromonomer synthesis was used only in few cases**.**

3.2.2. Macromonomer synthesis via anionic polymerisation

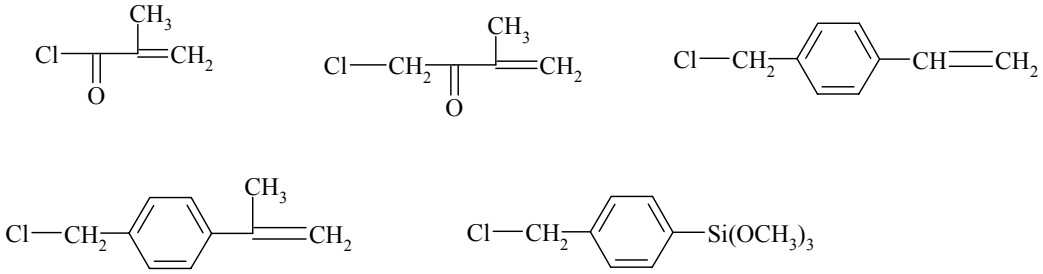
Well-defined macromonomers, of controlled chain length can be prepared in the anionic system. The first macromonomers based on polystyrene obtained using this polymerisation technique were synthesized by Milkovich [33-35]. Since that pioneering work almost all

categories of monomers able to polymerise anionically have been used for the macromonomers synthesis [44, 49-50].

By employing anionic polymerisation a terminal functional group can easily be introduced into the molecule. The most commonly used reactive end groups are unsaturated vinyl groups – vinyl benzyl and methacryl [44-45]. Generally, they can be introduced into polymer chain in two ways by an anionic initiator or by end capping of the *living* macroanion, however other methods were also successfully applied [44-68]. As the subject of this work is the synthesis and polymerisation of unsaturated macromonomers, the other type end groups (for example hydroxyl, carboxylic or ring-opening polymerizable groups) will not be discussed.

3.2.2.1. *End-capping* (termination) of a *living* polymer

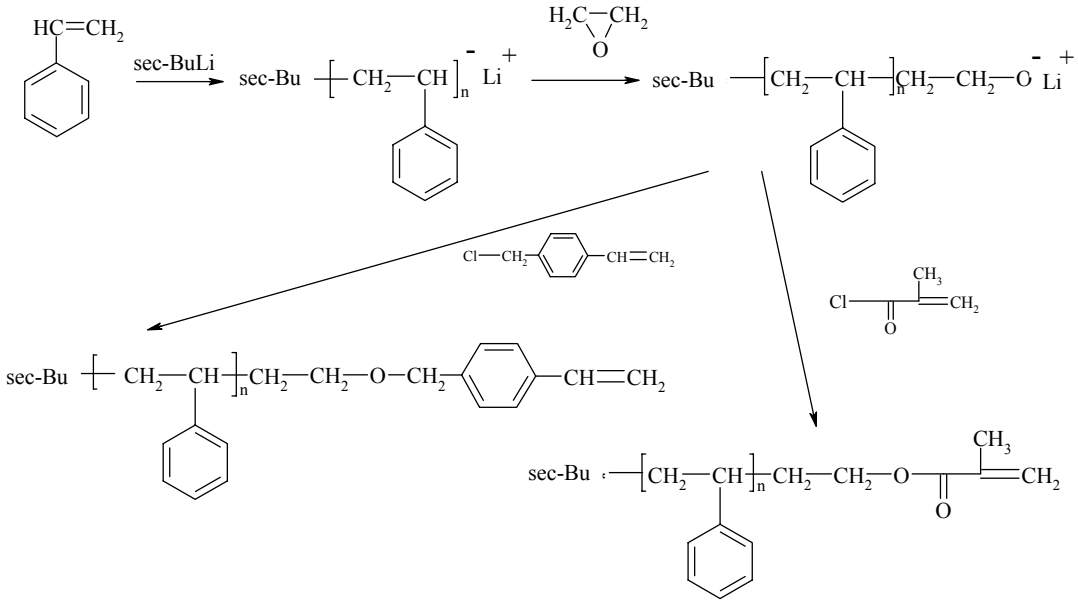
The deactivation of *living* anionic sites by an unsaturated electrophile turns out to be the privileged method of synthesis. However, the selection of the appropriate electrophilic unsaturated reactant should be made with care so as to avoid side deactivation reactions of the *living* polymer chain without introduction of polymerizable group. Generally, four types of electrophilic functions, which are alkyl halides, benzyl halides, chlorosilanes, and acyl chlorides have been successfully used for this purpose [44, 50]. Some examples are presented in Scheme 3.1.



Scheme 3.1. Typical termination agents.

However, depending upon the nucleophilicity of the anionic species to be deactivated and the electrophilicity of the terminating agent to be introduced at chain end, it is necessary in some cases to reduce the basicity of the *living* anions before deactivation. In order to transform growing carbanions into less nucleophilic anions prior to functionalisation such compounds as diphenylene and ethylene oxide were used [33-35].

For example in case of vinyl benzyl-type polystyrene macromonomers the direct termination of the *living* carbanion end with benzyl halide competed with a side reaction involving the attack of the carbanion at the double bound of *p*-benzyl halide. In order to suppress the side reaction Milkovich [33-35] first converted the *living* end of PS prepared by anionic polymerisation into an alcoholate end by the reaction with ethylene oxide (Scheme 3.2.). Than, the intermediate was reacted with methacryloyl chloride or vinylbenzyl chloride to give the final product. Therefore, the poly(styrene) (PS) macromonomer obtained by this method had an ether linkage between the end group and poly(styrylethyl) groups.



Scheme 3.2. Synthesis of poly(styrene) macromonomers by termination method according to Milkovich [33-35].

However, the synthesis of poly(styrene) macromonomers without change of nucleophilicity of *living* macroanion end was also described in the literature. The direct coupling of the polystyrene *living* end with *p*-benzyl halide was studied by Asami [50]. The coupling reaction of polystyrene lithium with excess *p*-vinylbenzyl chloride at –78 °C in a THF-containing solvent prevented the side reactions and macromonomers with high functionality were obtained. Although it was considered that carbanions of the *living* polymer could react with both the double bond and the chloromethyl group of *p*-vinylbenzyl chloride, a model reaction of *sec*-butyllithium with *p*-chloromethylstyrene showed that the reaction of carbanions with chloromethyl group was much faster than the addition of carbanions to the vinyl group.

Apart from styrene the termination of anionic *living* end of other polymers of alkyl methacrylates [51], or 2-vinylpirydine with a vinylbenzyl (or isopropenylbenzyl) halide [52]

gave the vinyl benzyl-type macromonomers. In all cases, the direct termination gave quantitative introduction of the polymerizable function at the chain end.

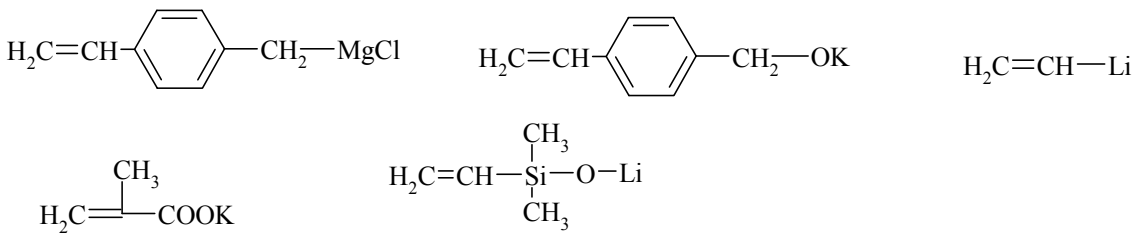
Preparation of methacryl-type macromonomers by terminator method was started by Milkovich [33], however similarly to PS-based macromonomers first *living* macroanions were converted into alcoholate followed by the *end-capping* with methacryloyl chloride (see Scheme 3.2.). Similarly, poly(styrene), or *2*-vinylpyridine methacryl-type macromonomers were prepared by Asami [53] and Rempp [54]. However, in case of *4*-vinylpyridine the direct termination of *living* chain gave well-functionalized macromonomers [55].

In case of polar monomers such as methyl methacrylate, it is generally difficult to obtain macromonomers with high functionality and narrow molecular weight distribution by anionic methods as the result of side reactions such as the anionic attack on carbonyl groups. Nevertheless, some macromonomers were prepared at low temperature, where the side reactions are significantly suppressed [56].

It should also be mentioned that the anionic polymerisation can also be an useful tool in the preparation of block macromonomers. In such synthesis the sequential monomer addition is applied. After the first monomer is reacted, the second monomer is introduced and finally the proper terminating agent. Such procedure was applied for example by Ishizu, who synthesized poly(methylstyrene)-*block*-poly(*2*-vinylpiridine) vinylbenzyl-type macromonomers [50].

3.2.2.2. Initiation by the compound carrying reactive group

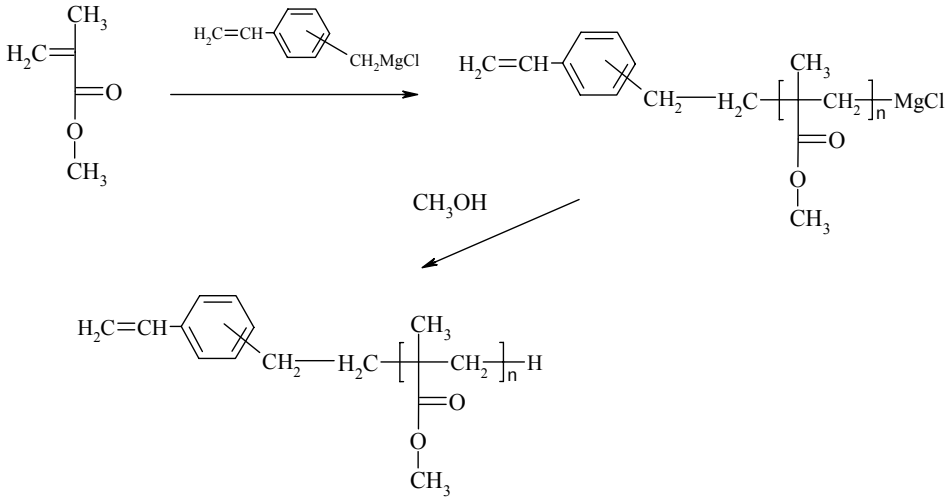
In few cases also unsaturated anionic initiators were used in order to synthesize macromonomers, however, only few macromonomers were prepared using this method. The number of such initiators is limited, because of difficulties to find compounds endowed with both polymerizable group and a function able to trigger an anionic process [57-58]. Some examples of used initiators are presented in Scheme 3.3.



Scheme 3.3. Unsaturated initiators used in anionic *living* polymerisation.

Not all types of monomers polymerizing anionically can be used by this method. The monomers suitable for macromonomer synthesis using anionic polymerisation with unsaturated initiator method are compounds containing oxiranes, siloxanes, lactones, or lactam rings. The anions generated with these monomers are weak nucleophiles unable to attack the double bond of the initiator. For instance, ring-opening polymerisation of *ε*-caprolactone initiated by lithium isopropyl-benzoxide [59] or polymerisation of hexamethylcyclotrisiloxane using lithium triethylsilanolate [60] resulted in well-defined compounds.

The application of an unsaturated initiator to polymerise vinyl monomers can be considered only if side reaction between initiator double bond and the growing anionic chain have little chance to occur. For instance, *p*-vinylbenzylmagnesium chloride was applied as an initiator for polymerisation of styrene, methyl methacrylate (Scheme 3.4.) and *4*-vinylpyridine to give vinyl benzyl-type macromonomers [61].

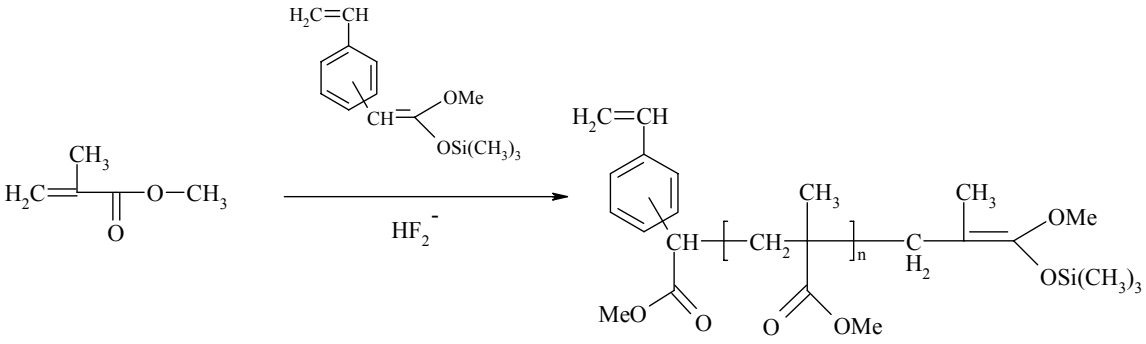


Scheme 3.4. Synthesis of poly(methyl methacrylate) macromonomers via unsaturated initiator method [61].

3.2.2.3. Group transfer polymerisation *(GTP)*

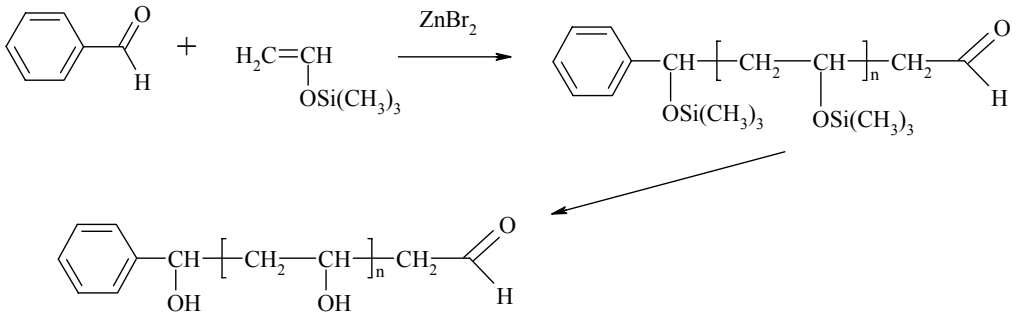
As it was mentioned it is difficult to obtain macromonomers with high functionality and narrow molecular weight distribution by anionic methods with regard to polar monomers. The side reactions appearing upon initiation step lead to multiplicity of the initiator moieties as well as to non active adducts of monomer and initiator. However, Webster *et. al*. developed a new synthetic method called “group transfer polymerisation” [62-63]. In this method silyl acetal initiates the polymerisation of polar acrylic monomers such as methyl methacrylate in the

presence of bifluoride anions. The resulting ketene silyl acetal group, can be used to the introduction of various functional groups at the end of the polymers. For example the synthesis of poly(methyl methacrylate) macromonomer by *GTP* with unsaturated initiator (vinylphenylketene methyl trimethylsilyl acetal), where the vinyl groups were introduced quantitatively to the macromonomer molecule with narrow molecular weight distribution presented in Scheme 3.5. was reported by Asami *et al.* [64].



Scheme 3.5. Synthesis of poly(methyl methacrylate) macromonomer via group transfer polymerisation [64].

Another type of group transfer polymerisation by means of silyl aldol condensation presented also by Webster *et. al*. [65] includes the use of Lewis acids (such as zinc bromide) as catalysts. The obtained polymer was subjected to hydrolysis to yield poly(vinyl alcohol) with an aldehyde end group, as presented in the Scheme 3.6.



Scheme 3.6. Silyl aldol condensation [65].

3.2.2.4. Other methods

Inoue *et al.* have reported that some aluminum porphirins can initiate the ring-opening polymerisations of epoxides [66], or lactones [67] and called this system “immortal”. Using this method they prepared vinyl benzyl-type polyester macromonomer [68]. However, the application of this type of polymerisation is limited.

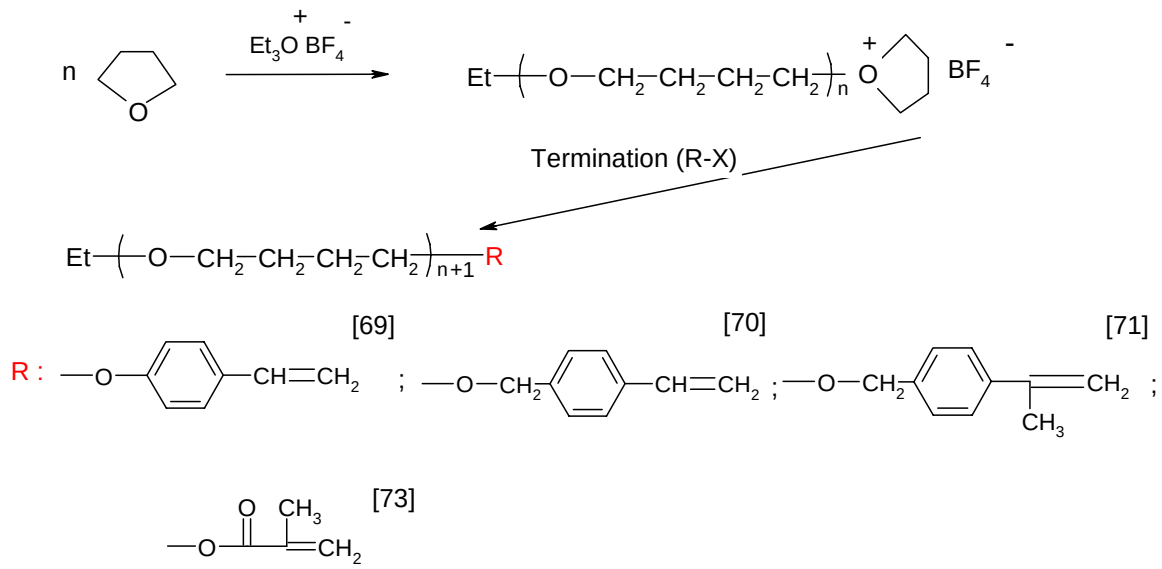
3.2.3. Macromonomers synthesis via cationic polymerisation

Both initiating and end-capping methods were used for the synthesis of macromonomers using cationic polymerisation. Though, in contrast to anionic polymerisation, not many monomers can be polymerised cationically under living conditions.

3.2.3.1. *End-capping* (termination) of a *living* macrocations

The termination of *living* macrocation with a nucleophile having a polymerizable group is a versatile method to prepare THF-based macromonomers. The ring-opening polymerisation of tetrahydrofuran initiated with triethyloxonium tetrafluoroborate followed by the termination with unsaturated nucleophile (sodium *p*-vinylphenoxide [69], sodium *p*-vinylbenzoxide [70], or potassium *p*-isopropenylbenzyloxide [71]) led to the poly(THF) macromonomers possessing unsaturated double bond (Scheme 3.7.).

Also introduction of methylacryloyl group into polymer chain is possible by the termination of *living* carbanion with methacrylic acid or its salts. In such ways methacryl-type polyamine macromonomers [72] as well as poly(tetrahydrofuran) macromonomers [73] were prepared (Scheme 3.7.).

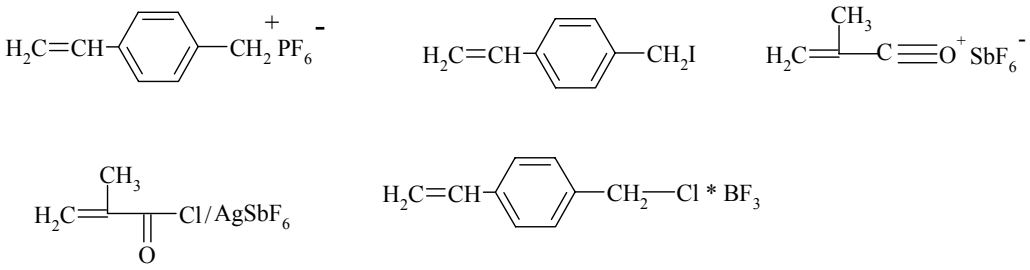


Scheme 3.7. Synthesis of poly(THF) macromonomers by termination method.

In the ring opening polymerisation of *2*-oxazolines vinyl benzyloyl-, acryloyl- as well as methacryloyl groups were introduced by the end-capping methods giving macromonomers with well-defined structure and high end group functionality [74-75].

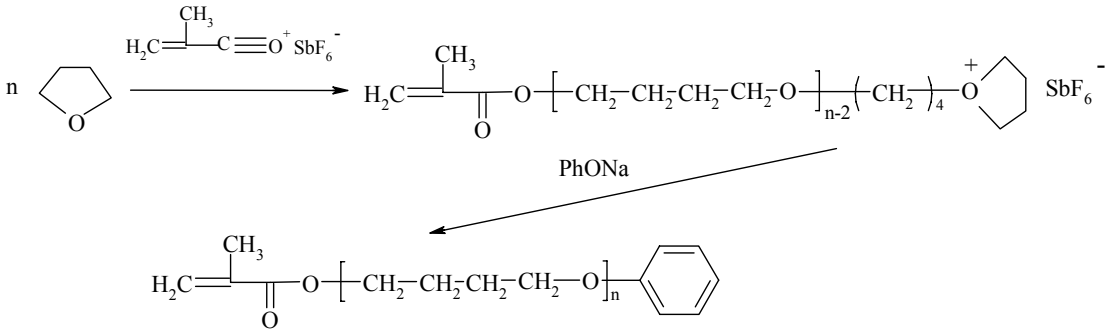
3.2.3.2. Initiation by the compound carrying reactive group

Compounds containing a methacryl group as well as vinyl benzyl group have been successfully used as initiators for preparation of macromonomers by cationic polymerisation. Some examples are presented in Scheme 3.8.



Scheme 3.8. Unsaturated initiators of cationic polymerisation.

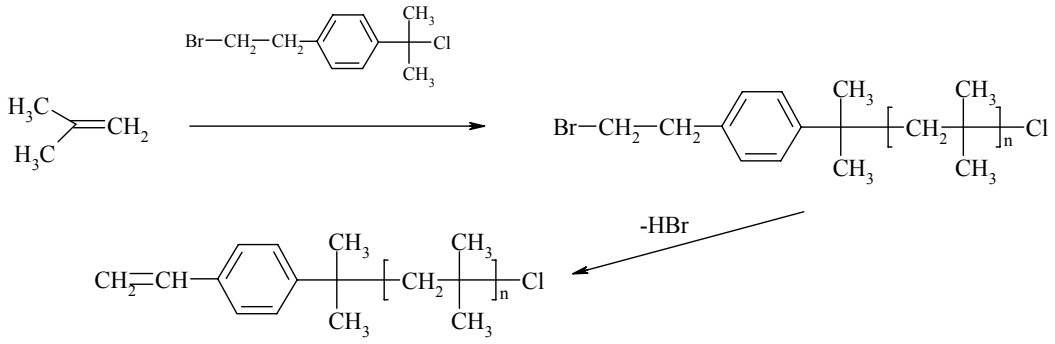
A typical example of macromonomer synthesis using cationic initiation method is the synthesis of poly(tetrahydrofuran) macromonomers. By application of different types of cations, such as methacryloyl cations [76], or methylstyrene cations [77] vinyl benzyl- or methacryl-type macromonomers can be obtained, as presented in the Scheme 3.9.



Scheme 3.9. Synthesis of poly(THF) macromonomers via unsaturated initiator method [76].

Cationic polymerisation of epichlorohydrin in the presence of allyl alcohol or *2*-hydroxyethyl acrylate gave macromonomers having an allyl- or acyl- terminal group, respectively [78].

Kennedy *et al.* developed the so-called "inifer" (initiator-transfer) method by which various macromonomers were synthesized from polyisobutene. With this method, for example a vinyl benzyl-terminated macromonomers were formed [79]. The *p*-(2-bromoethyl)cumyl end groups of well-defined polyisobutylene (polymer resulting after cationic polymerisation of isobutene initiated by *p*-(2-bromoethyl)cumyl chloride) were transformed into vinyl benzyl groups by dehydrobromination as presented in Scheme 3.10.



Scheme. 3.10. "Inifer" (initiator-transfer) method as the way to macromonomers.

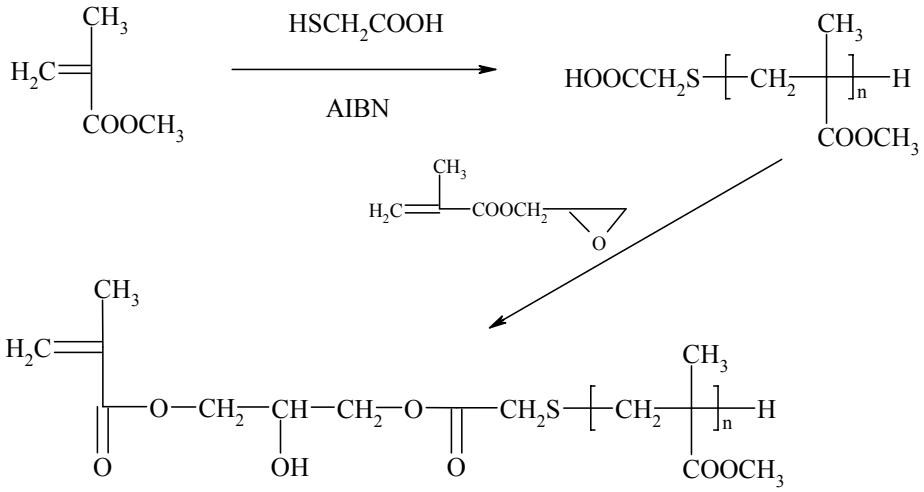
Nevertheless, the molecular weight distributions of macromonomers obtained from these cationic methods are wider than of those synthesized via anionic polymerisation, which usually proceeds according to the *living* mechanism. Generally, during the presented initiating method reactions the presence of polymerizable functional groups is unavoidable, what leads to side reactions. It decreases the degree of functionality of the resulting macromonomer, as well as increases its dispersity index. As the result only few well-defined, narrow distributed macromonomers were obtained according to cationic *living* mechanism [80].

3.2.4. Macromonomers synthesis via radical polymerisation

In comparison with cationic or anionic polymerisation, in particular *living* polymerisations, radical polymerisation gives polymers with relatively wide dispersity indices, what sometimes makes the molecular design difficult. Nevertheless, radical polymerisation has been wildly applied to produce macromonomers because of its practical simplicity. Even monomers able to a *living* polymerisations such as styrene or methyl methacrylate have been subjected to the above procedure because the ionic processes involve very stringent conditions. Additionally, many vinyl monomers can not be polymerised by *living* polymerisations thus there is no other possibility as to prepare macromonomers in radical processes.

However, in order to obtain the macromonomers by radical polymerisation it is necessary to control the mechanism of polymerisation (*ATRP, GTP*). Two steps are generally required to obtain macromonomers via radical polymerisation. The first step includes the synthesis of ω-functional polymers. It can be achieved by the use of an appropriate transfer agent or from a functional initiator bearing transferable group. The second step consists of introduction of the unsaturation using the terminal functional groups, what is usually achieved by reaction with an unsaturated compound carrying an antagonist function.

Thiol compounds are often applied transfer agents during polymerisation of acrylic monomers. The most commonly used is thioglycolic acid, which was applied for synthesis of macromonomers from methyl methacrylate [81-82] (Scheme 3.11.), stearyl methacrylate [81], *2*-dimethylaminoethyl methacrylate [83], or *2*-acetoxyethyl methacrylate [84-85]. As the result of chain transfer polymerisation, the polymers with terminal carboxyl groups were obtained. As next, in order to introduce unsaturated methacrylic end group, the mentioned polymers were reacted with glycidyl methacrylate, where for the preparation of vinyl benzyl- terminated macromonomers, carboxyl-terminated poly(methyl methacrylate) and poly(*2*-acetoxyethyl methacrylate) were reacted with *p*-vinylphenyl glycidyl ether [84-85]. It should be mentioned that the second step of macromonomers synthesis requires a relatively high temperature, which is sometimes undesirable for the preparation of macromonomers having special functional groups.



Scheme 3.11. Synthesis of poly(methyl methacrylate) macromonomer by chain transfer polymerisation [81-82].

In the synthesis of polystyrene macromonomers, instead of thioglycolic acid iodoacetic acid is applied as the chain transfer agent. The resulting prepolymer is used for preparation of macromonomers with methacrylic or styrene group by modification of carboxylic group [86].

Similar to the described procedure to the synthesis of several macromonomers from monomers such as vinylpyrrolidone [87], acrylamide [87], or vinylchloride [88] were applied.

A single-step preparatory method in the macromonomers synthesis was also developed. Allyl sulfides with ester, phenol or cyano groups attached to the double carbon bonds were used during such synthesis. By application of such chain transfer agents, polystyrene or

poly(methyl methacrylate) macromonomers with high molecular weight and high functionality were easily prepared [89].

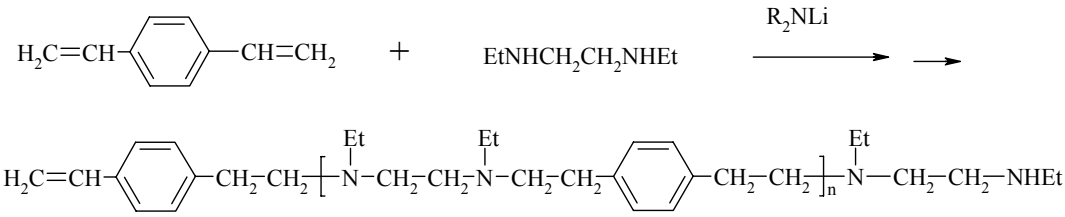
Matyjaszewski *et al.* as first reported the application of *ATRP* polymerisation (will be discussed later) to one-step macromonomers synthesis. By using different halogen unsaturated initiators such as vinyl chloroacetate [90] and allyl bromide [91] he obtained well defined polystyrene macromonomers. However, the mentioned initiators were not active in the preparation of methacrylates (for example methyl methacrylate).

This problem was solved by Shen *et al*. who applied other vinyl initiators (vinyl chloroacetate, vinyloxyethyl 2-bromoisobutyrate and vinyloxypropyl trichloroacetamide) which were active in the synthesis of poly(methyl methacrylate), methyl acrylate as well as of polystyrene macromonomers [16]. All the obtained macromonomers exhibited high functionality and narrow dispersity indices, however, in case of acrylate macromonomers, reaction must have low conversion of monomer due to side reactions (branching by incorporation of initiator molecule into the main chain of the macromonomer).

3.2.5. Macromonomers synthesis via step-growth processes (polycondensation or polyaddition)

When the polycondensation reaction is carried out under stechiometric conditions (equal amount of both monomers) obtained (AA + BB)-type polycondensates resulting from step-growth processes are fitted with antagonist function at each of their extremities. If one of the initial reactants is a divinylic compound, ω-unsaturated polycondensates are formed. This strategy was applied in several cases to produce macromonomers, especially to the one containing vinyl or acryloyl terminal groups.

Polyamine macromonomers end-fitted with a vinyl benzyl unsaturation have been obtained by Tsuruta [92-93]. He reacted divinylbenzene and *N,N'*- diethylene diamine in the presence of lithium amide. The adduct resulting from the attack of the vinyl benzyl unsaturation by lithium amide transfers its charge to a secondary amine of another molecule, which in turn adds a new unsaturation, as presented in Scheme 3.12.



Scheme 3.12. Synthesis of polyamine macromonomers by polycondensation reaction.

The other example of step-growth reaction can be the synthesis of acrylamide-type macromonomers applying Michael-type polyaddition of diacrylamide compounds. For example, the addition of *1,4*-bis-acryloylpiperazine and *N,N'*-dimethylethylenediamine produced poly(amideamine) macromonomer [94].

3.2.6. Macromonomers from *ω*-functional polymers

As it was mentioned in case of preparation of macromonomers by radical polymerisation, sometimes the synthesis of macromonomers in one step process is problematic. Additionally, the initiation or termination of *living* chain in cationic or anionic *living* polymerisations leads also not always to the macromonomers with high degree of functionality. In such cases the modification of *ω*-groups from the polymer chain obtained by one of the mentioned mechanisms in direction of desired groups seems to be useful.

Terminal functional groups such as carbonyl, hydroxyl or amino groups, appearing after polymerisation of the monomer at the end of the chain, are the example of such transformable groups in direction of unsaturated groups. From the point of view of further modification, it is not important which technique was chosen to the preparation of *pre*-polymers used for further modification. However, taking into account the future application of the macromonomers, where narrow distributed polymers are usually desired, the polymers prepared by *living* polymerisation techniques like anionic or cationic are preferable. However, as it was already presented, in case of some monomers the application of this techniques is not possible or problematic. In those cases the modification of radically obtained polymers can be applied.

The type of end group available for modification is dependent from the chosen monomer as well as from the way of termination (compound used as terminator). In order to obtain well defined macromonomers it is important so that only *ω*-placed transformable group underwent the modification. As the result not all kinds of macromonomers can be prepared using this method. The way of synthesis exclude the application of the monomers having in its structure

the group able to modification, like for example poly(vinyl alcohol) or poly(glycidol) carrying hydroxyl group.

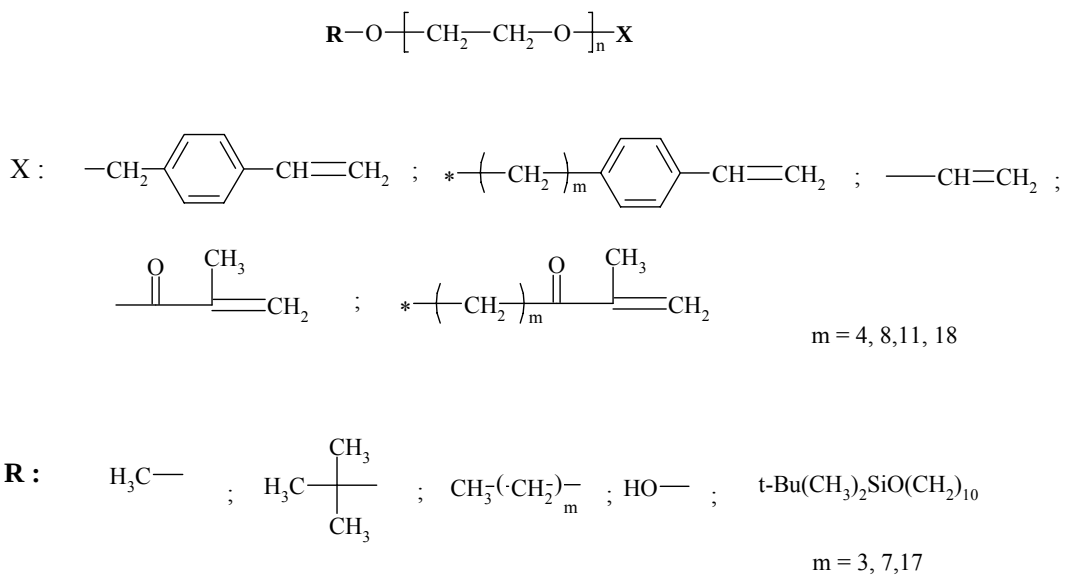
Some examples of modification of ω-terminated polymers were described in the chapter dealing with the synthesis of macromonomers by radical polymerisation. The modification of ω-functional polymers was also wildly used for the preparation of polyethylene oxide macromonomers, whose synthesis will be described in details in the next chapter.

The modification of hydroxyl group by the reaction with methacryloyl chloride in the presence of amine led to methacryl-type macromonomers of such polymers as poly(oxazoline) [95], or poly(isobutene) [96]. As reported by Mikesova *et al.* methacrylate-terminated polyurethane macromonomers can be synthesized by the reaction of isocyanate-terminated polyurethane (formed by the reaction of diisocyanate compounds with poly(oxytetramethylenoxyadipoyl)) and *2*-hydoxyethyl methacrylate [97]. In contrast, as the vinylbenzyl chloride was used to modification, the vinyl benzyl-type macromonomers of poly(methyl methacrylate) were easily obtained [44].

3.2.7. Synthesis of poly(ethylene oxide) macromonomers

Poly(ethylene oxide) (PEO) is the well-known, water-soluble, nonionic polymer, which was used, among the variety of other application, for the preparation of macromonomers. Its macromonomers have been the subject of many publications. The synthesis of well-defined graft copolymers by copolymerisation of PEO macromonomers with conventional monomers [37, 52, 98, 99], as well as the synthesis of regular comb-like polymers by their homopolymerisation was described [21-24]. The most important and interesting feature of PEO macromonomers is their amphiphilic nature. In principle, they are soluble in a wide range of solvents like water, alcohols, benzene, chloroform, THF. Nevertheless, their solubility depends also on the nature of the end groups and the length of the main chain. Additionally, the other important feature of PEO-macromonomers is their ability to self-organization in selective solvent (for instance water) [21-24].

The schematic structure of poly(ethylene oxide) macromonomer is presented in the Scheme 3.13., where *R* corresponds to the reactive, usually unsaturated polymerizable group, and *X* is the other end group usually inactive in the polymerisations reactions.



Scheme 3.13. Examples of PEO-type macromonomers.

A variety of PEO-macromonomers with a variety of end groups and molecular weights was prepared. However, in this work mostly the synthesis of PEO-macromonomers bearing unsaturated end group (methacryloyl, vinyl benzyl, or acryl) will be presented. The prevailing synthesis rout seems to be anionic polymerisation of ethylene oxide. The reactive group is usually introduced by termination of *living* chain with compound carrying the unsaturation, or by modification of ω-hydroxyl group of resulting polyethylene oxide. Examples are presented in Scheme 3.13.

3.2.7.1. By anionic *living* polymerisation (termination or initiation method)

The PEO macromonomers having at one chain end methyl, *tert*-butyl, *n*-butyl, or *n*-octyl group and at the other chain end acryloyl, methacryloyl, or *p*-vinylmethyl styrene group were synthesized via anionic polymerisation of the monomer followed by termination with the corresponding chloride [52, 98, 100-102]. The conditions of this reaction seems to be well established. The corresponding potassium alkoxides were used as initiators of polymerisation of ethylene oxide in THF at 40 °C. The conversion of the monomer was almost quantitive after about 16 hours what led to polymers with the desired composition. The compounds obtained using this method showed narrow molecular weight distribution and well-defined ω- and α- functionality.

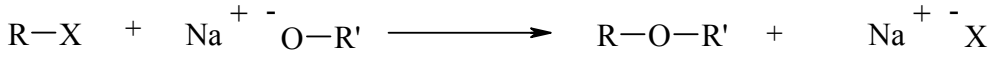
ω-Hydroxyl macromonomers of vinyl benzyl- or methacryl-type were also obtained by anionic polymerisation of ethylene oxide. As initiator *t*-butyldimethylsilyl protected alkoxides were used. After termination with appropriate chloride the desilylation reaction with tetra-*n*-butylammonium fluoride gave deprotected macromonomer [24].

The example of the PEO macromonomer bearing the other unsaturation group can be the work of Kobayashi *et. al* [103]. Anionic ring-opening polymerisation of ethylene oxide by lithium salt of *2*-(hydroxyphenyl)-*2*-oxazoline produced poly(ethylene oxide) macromonomers bearing polymerizable *2*-oxazoline group. The molecular weight was controlled by varying the feed ratio.

3.2.7.2. By modification of *ω*-hydroxyl group

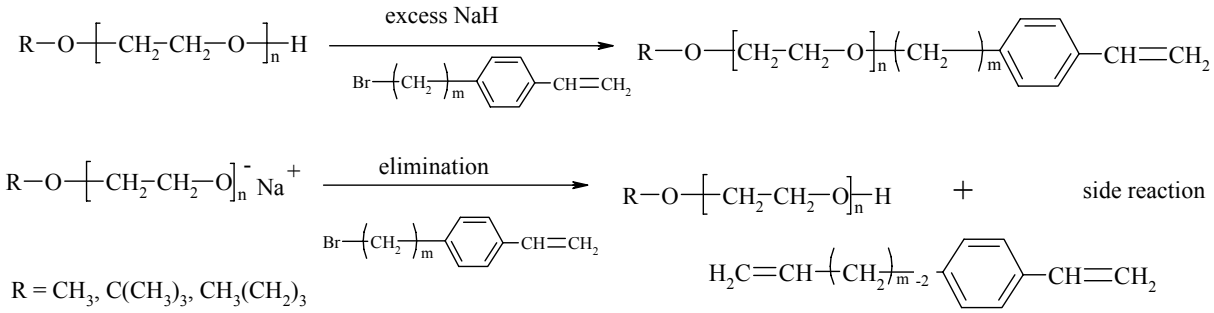
The modification of hydroxyl group of commercially available poly(ethylene oxide) monoalkyl ethers was also used for preparation of macromonomers [104-105]. However, the application of this method is limited to the well defined polymers, where the hydroxyl group is placed only at one chain end. Any traces of poly(ethylene glycol) would lead to telechelic difunctional macromonomers.

The commonly used reaction for the preparation of vinyl benzyl- and methacryl-type PEO macromonomers of high functionality [104,105] is Williamson's synthesis presented in the Scheme 3.14. [106]. The alkoxidation of the *ω*-hydoxyl poly(ethylene oxide) with sodium or sodium hydride leads to the poly(ethylene oxide) alcoholates, which are active in the coupling reaction with alkyl halide (bromide or chloride).



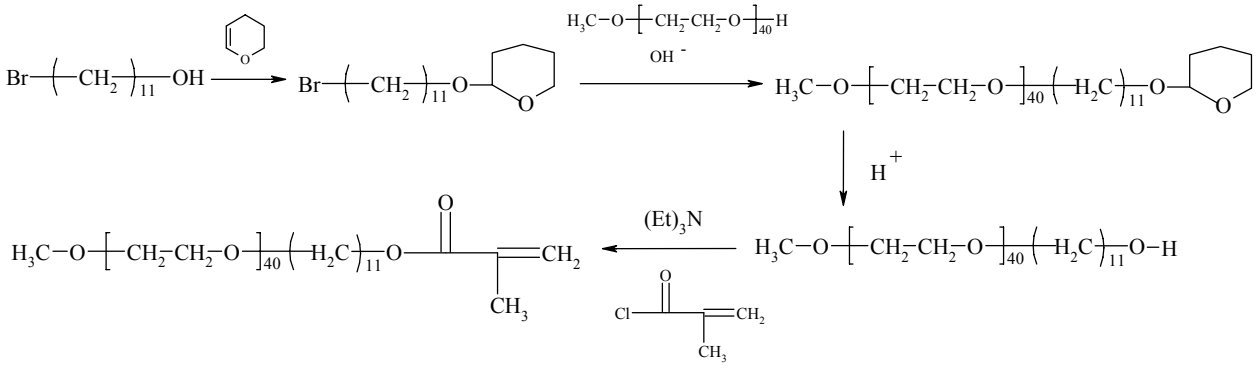
Scheme 3.14. Williamson's synthesis.

The vinyl benzyl group containing "so called" spacer of the short alkyl chain (4, 8, 11, or 18 carbon atoms) was also introduced to the polymer chain of poly(ethylene oxide) macromonomers by Williamson's synthesis. However, this time 5-mol fold of *p*-vinyl benzyl alkyl bromide was required in order to convert all the hydroxyl groups, due to appearance of side reaction of elimination, as presented in Scheme 3.15. [21].



Scheme 3.15. Synthesis of vinyl benzyl-type poly(ethylene oxide) macromonomer with alkyl spacer.

In contrast highly functionalized methacryl-type macromonomers with hydrophilic spacer were prepared by two step reaction (Scheme 3.16.). As first an alkyl spacer was introduced to the polymer chain by the modified Williamson's reaction, followed by the esterification of the resulting hydroxyl group with methacryloyl chloride [101].



Scheme 3.16. Introduction of methacrylate group with spacer to poly(ethylene oxide) chain.

3.2.8. Characterization and purification of macromonomers

The properties of macromonomers which are important for the further synthesis of graft copolymers or polymacromonomers are: purity (the degree of functionality), molecular weight, molecular weight distribution and solubility. As it was presented macromonomers synthesized by *living* polymerisations usually demonstrate desired properties while whose obtained by radical polymerisation or cationic polymerisation usually are the mixture of non- and functionalized polymer.

The technique which is commonly used for the estimation of molecular weight and molecular weight distribution of macromonomers is size exclusion chromatography (*SEC*) [21-24, 40-45]. The degree of polymerisation of macromonomer can be estimated as the ratio of obtained

value and the molecular weight of mer. However, this method fails in estimation of the functionality of the macromonomer.

A fast method allowing to check if the macromonomer is fully functionalized or is the mixture of non- and functionalized form is *MALDI-TOF-MS* [107]. In case of fully functionalized macromonomers only one distribution or distributions (for instance sodium and potassium) assigned to the macromonomer bearing functional group will be found on the mass spectra. In contrast for the sample which is a mixture of non- and functionalized macromonomer distributions deriving from both oligomer as well as macromonomer will be present on the spectra. However, as this method is not quantitive, the degree of functionality can not be determined.

One of the methods used to quantitive estimation of the degree of polymerisation is *^{1}H NMR*, but only if the peaks of the main chain are separated from those of the end and initiator groups [108]. The degree of the functionality is then calculated as the integral ratio between the end group and initiator group. However, as the degree of polymerisation of macromonomer increases the precise determination of integrals of the terminal groups can be complicated and the error of this method increases.

UV analysis seems to be the most precise means of determining the amounts of terminal macromonomer groups. The amount of end group i.e. vinyl benzyl end group can be analysed by means of *UV* spectrum compared with that of model compound i.e. *p*-methyl styrene [50, 73].

Moreover *IR* was used to calculate the concentration of the end groups of macromonomer in comparison with that for model compound [108], also to high molecular weight polymers.

It is usually difficult to apply conventional purification methods such as precipitation in order to separate the polymer with the terminal polymerizable group from non-functionalized as they show similar solubilities. As the result usually the mixture of functionalized and non-functionalized macromonomer is used to polymerisation and then the polymacromonomer is purified.

3.3. Synthesis of polymer bottle-brushes by homopolymerisation of macromonomers

As it was shown in the previous chapter a large number of macromonomers differing in the type of the repeating monomer and the end group have so far been prepared. This opens the way to an enormous number of branched polymers in a variety of architectures and compositions [109]. The polymer bottle-brushes are one of the example of the structures, which can be obtained by macromonomer technique. However, since macromonomers are already polymers their polymerisation proceed differently then the polymerisation of corresponding low molecular weight monomers.

As a matter of fact, all the main polymerisation technique like cationic, anionic, or radical were successfully applied in homopolymerisation of macromonomers. However, there have been only few reports on controlled polymerisation techniques including both the cationic [47] and anionic polymerisation method [47, 110-111] or controlled radical polymerisation like atom transfer radical polymerisation (*ATRP*) [19]. The main reason of the lack of interest in this techniques are the problems with purification of macromonomers from undesired low molecular weight compounds like traces of terminator, contaminations of solvent or monomer used for polymerisation or salts. It is hard or impossible to obtain pure macromonomer in traditional ways like by distillation (too high molecular weight) or precipitation (usually to low molecular weight). Also the application of dialysis is possible only for the macromonomers whose molecular weight exceed the exclusion limit of the available membranes.

As the result the traditional chemical pathway to cylindrical brushes is the radical polymerisation of macromonomers [21-24, 113-116]. The major advantage of this technique is its simplicity and relatively high tolerance to impurities present in the system. In most cases macromonomer purification is not required to a high extent and initiator residues do not need to be removed from the polymer, because they have little or not influence on polymer properties. Additionally, this technique is adaptable to many types of end-groups of macromonomers under mild conditions using convenient and not sophisticated equipment and initiators. Moreover, from the industrial point of view radical polymerisation processes can be readily and economically performed.

However, conventional radical polymerisation has also a big disadvantage, the precise control over chain growth is impossible. The decomposition of initiator is slow so the polymeric chains are initiated in different time, what decreases their uniformity. Additionally, because of lack of control over chain breaking reactions, i.e. both termination and transfer steps greatly limit the ability to control polymer architecture. As the result control over molecular weights is impossible and broad polydispersed products are usually obtained. Thus, such polymers tend to contain significant amounts of high and very low molecular weight chains, which can influence the properties of the final product.

3.3.1. Homopolymerisation of macromonomers

The polymerisation system of macromonomers differ from the polymerisation system of small monomers and in general, can be characterized by low concentration of the polymerizable end group and high viscosity of the polymerisation media from the beginning of the polymerisation [20]. The propagating step is then a repetition of a polymer-polymer reaction where formed specific multibranched structure shows high segment density around the propagating radical. Additionally, distribution of reaction species in the polymerisation media becomes often heterogeneous due to the interaction between polymer chains or polymer and solvent.

The mentioned features enhance diffusion controlled effects. Therefore, macromonomer polymerisation is usually sensitive to the diffusion-controlled step of the polymerisation reaction. The properties of polymacromonomer radicals differ markedly from those of linear radicals, what usually influence the maximum attainable degree of polymerisation and the polymerisation kinetics of macromonomers.

3.3.1.1. Rate of polymerisation (R_p) in non-polar solvent (benzene)

Taking into account kinetics of the radical polymerisation, the overall rate of the polymerisation of macromonomers is equal to the rate of propagation step. R_p, can be expressed as presented in equation 3.7.

$$R_p = -d[M]/dt = k_p[P\cdot][M] \qquad \textbf{(3.7.)}$$

where k_p is the rate constant of propagation while *[M]* and *[P•]* are the concentration of macromonomer and propagating radical, respectively.

The rate of termination (R_t) and initiation (R_i) in this process can be expressed as presented in equations 3.8. and 3.9,

$$R_t = -d[P\cdot]/dt = k_t[P\cdot]^2 \quad \textbf{(3.8.)}$$

$$R_i = 2k_d f[I] \quad \textbf{(3.9.)}$$

where *[I]* is initiator concentration, k_t and k_d are rate constants of termination and initiation reactions, respectively; and *f* corresponds to the initiator efficiency.

Taking into account the equations 3.8. and 3.9. and assuming the steady-state ($R_t = R_i$ so that the concentration of radicals in the system was constant) the kinetic of the propagation step of macromonomers polymerisation can be presented as in the equation 3.10 [112].

$$R_p = k_p\left(\frac{2k_d f}{k_t}\right)^{0,5} * [I]^{0,5} * [M] \quad \textbf{(3.10.)}$$

Radical polymerisation rate of macromonomers and its dependence on initiator and macromonomer concentration have been investigated by several authors [20-21, 24, 70], however, the most detailed studies of many aspects of macromonomers polymerisation were presented by Tsukahara *et al* [113-116], who compared the polymerisation rate of methacryl-type and styryl-type macromonomers during radical polymerisation in benzene. The pairs of macromonomers with similar molecular weight, but different end group were investigated. It was noticed for all studied macromonomers that the R_p of polymerisation was decreasing monotonically as the polymerisation proceeded. The same observations were made for macromonomers with different concentration in polymerisation system, indicating that this feature is characteristic of the polymerisation of macromonomers [115].

It is in contrast to the polymerisation of small monomers in the present of gel effect [117]. Upon such reaction the overall rate of polymerisation decreases gradually with monomer conversion, however only to some moment. When the system reaches sufficiently high viscosity the mobility of the molecules is highly suppressed. The reactions in the system become diffusion controlled. Under such conditions the termination reaction is severely suppressed, while initiation and propagation proceed almost at the same rate as before (diffusion of small molecules is easier then of polymers). Thus, the number of growing chains is increasing, and the overall polymerisation rate accelerates enormously. However, in case of

macromonomers polymerisation the gel effect appears from the beginning of the polymerisation, thus acceleration of the polymerisation rate is observed at high conversions of macromonomers.

It was also observed by Tsukahara *et al.* [115] that the polymerisation reactivity of the end group bearing a long styrene chain influences R_p of macromonomers. The rate of polymerisation of methacryl-type macromonomers was substantially greater than that of vinylbenzyl-type. Additionally, if comparison was made at the same *[M]* of macromonomers the R_p increased with increase of the molecular weight of the macromonomer. However, it can be explained considering gel effect, as it gets greater as the molecular weight of the macromonomer increases. Nevertheless, the larger value of R_p was preserved above some concentration (presence of the strong diffusion controlled effect).

Different results were obtained by Asami *et al.* [70] who investigated the radical polymerisation of tetrahydrofuran macromonomers having vinylbenzyl- and vinylphenoxy- end group also in benzene. It was observed that at low concentrations, lower then *[M]* = $1{,}6*10^{-3}$ mol/L, the polymerisation of macromonomers proceed the same as that of conventional small vinyl monomers. However, above this concentration polymerisation rate of macromonomer was higher then for small monomer, similarly as observed by Tsukahara *et al.*

Also the influence of the initiator concentration (*AIBN*) *[I]* on the rate of polymerisation was investigated by Tsukahara *et al.* [114]. With respect to the polymerisation of macromonomers, the propagation reaction is the repeat of the polymer-polymer reaction in which the rearrangement of both the propagating chain and the macromonomer chain by segmental diffusion is required during each propagating step, to allow the close approach of the radical sites and the polymerizable end groups. Therefore, the polymerisation kinetics is influenced by the segment density around the propagating radical side. For the propagating radical of small degree of polymerisation that is formed at small *[M]* the bimolecular termination of polymacromonomer radicals can take place with little difficulty. However, at high initial concentrations of macromonomer the propagating radicals of large *DP* is formed and as the result the bimolecular termination becomes more difficult due to the high segment density around the radical site, what is schematically shown in Figure 3.2.

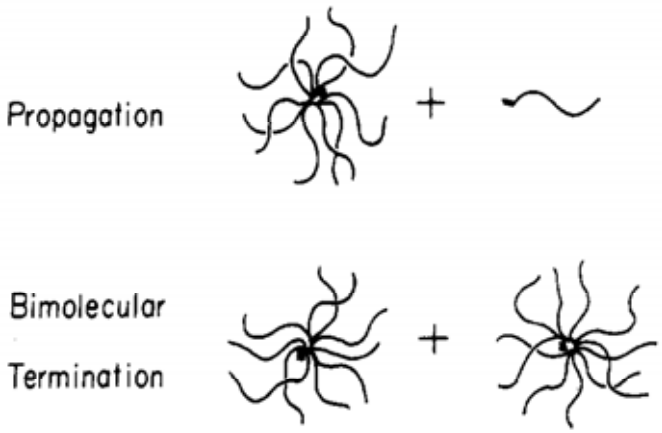


Figure 3.2. The propagation and the bimolecular termination reaction in the macromonomer system [113].

Thus, the unimolecular termination seems to be more important under such conditions, where the suppression of bimolecular termination is expected to be more pronounced at much higher concentrations of macromonomer. From the other side, the increasing viscosity of the polymerisation media can also enhance the cage effect, what promotes unimolecular termination. As the result of mentioned factors the observed kinetic order of macromonomers polymerisation with respect to *[I]* was almost 0,5 at low *[M]*, whereas at high *[M],* the order was much less than 0,5.

3.3.1.2. Degree of polymerisation of polymacromonomers

Homopolymerisation of macromonomers provides regular multibranched polymers presented in the Figure 3.3. with a high branch density, where for example for a vinyl type macromonomer the branch is situated on every second carbon atom.

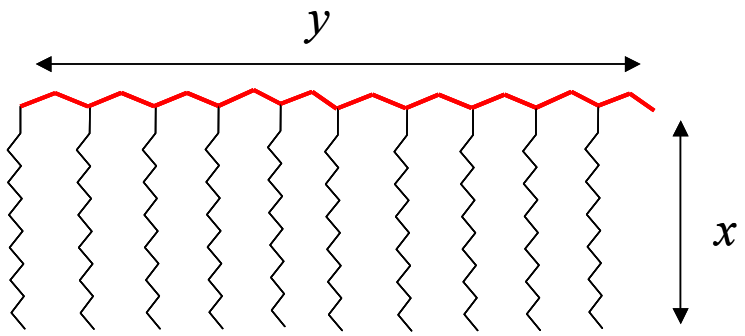


Figure 3.3. Schematic picture of polymacromonomer structure.

The characteristic parameters applied to the characterization of polymacromonomers are the length of branches *x* referring to the degree of polymerisation (*DP*) of used macromonomer and the length of backbone *y* referring to the *DP* of obtained polymacromonomer. It should be mentioned that this values are the average values as both the macromonomer and polymacromonomer are the mixture of polymers with different molecular weight.

A few years ago, the attainable *DP* of polymacromonomers was considered to be very low because of the mentioned steric effect associated with the specific multibranched structure of the propagating radical caused by an increase in the number of branches around the radical site, i.e., the degree of polymerisation of the propagating radical. The small *DP* of macromonomers (from 6 to 30) were reported by Asami *et al*. [70, 73] for both vinylbenzyl- and methacryl- poly(tetrahydrofuran) macromonomers, by Rempp *et al.* [118-119] for the corresponding polystyrene macromonomers and by Ito *et al.* [104] for PEO macromonomers. Better results were obtained by Hatada *et al.* [120] for vinylbenzyl poly(methyl methacrylate), where *DP* of polymacromonomers reached 60. Additionally, in all cases the conversion of macromonomer was not full and usually lower then 50 %, where in case of vinylbenzyl poly(methyl methacrylate) macromonomer not exceeded 12 %. In all cases polymerisation was carried out in benzene at 60 °C using *AIBN* as initiator.

The application of controlled polymerisation techniques also did not improve the results. Anionic polymerisation of methacryloyl polystyrene using sec-BuLi gave low degrees of polymerisation (≈ 30), similar to those obtained by radical polymerisation [118], where in the cationic polymerisation of vinylbenzyl poly(styrene) only oligomers were obtained [53].

The first one who reported high degrees of polymerisation of polymacromonomers during radical polymerisation of polystyrene macromonomers in benzene initiated with *AIBN* was Tsukahara *et al.* [113-116]. As he conduct systematic studies of polymerisation behaviour of macromonomers and presented the dependence of macromonomer conversion and *DP* of the polymacromonomers on such factors as molecular weight of macromonomer, type of the reactive end group, initial concentration of macromonomer and the amount of initiator, his work will be presented in details.

Four macromonomers were chosen to the investigation: two possessing vinylbenzyl end group with molecular weight 4980 g/mol and 13200 g/mol (VB-PSt4980, VB-PSt13200) and two possessing methacryloyl end group with molecular weight 4400 g/mol and 12400 g/mol

(MA-PSt4400, MA-PSt12400). The obtained results by Tsukahara *et al.* are presented in the Figure 3.4.

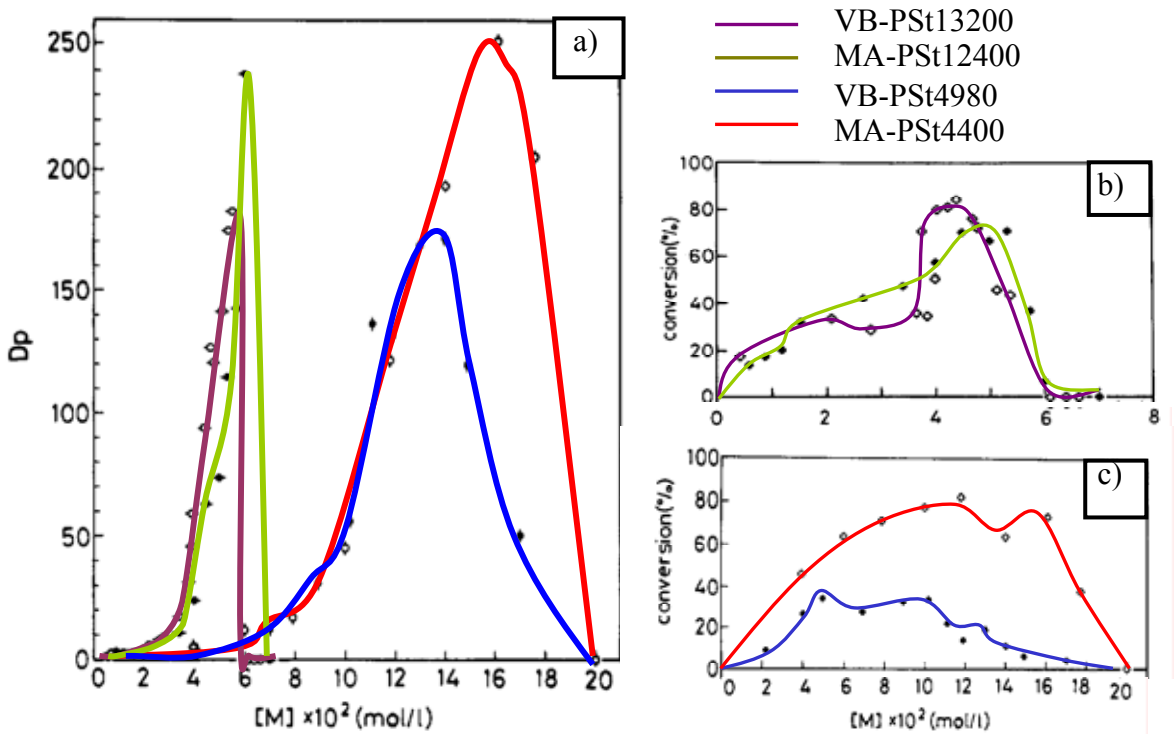


Figure 3.4. Comparison of *DP* versus *[M]* plots of polymacromonomers obtained from MA-PSt4400, MA-PSt12400, VB-PSt4980, VB-PSt13200 (a) and conversion versus *[M]* (b, c). Polymerisation in benzene at 60 °C for 24 h with *[I]* = 1,64 * 10^{-2} mol/L of *AIBN* [115].

It can be seen that the *DP* of the obtained products were strongly concentration dependent in a unique manner. For all the macromonomers the characteristic maximum was found on the obtained curve, however, the initial concentration, for which the maximal values of *DP* were obtained, depended form the molecular weight of the applied macromonomer. In case of macromonomers with higher molecular weight the complete suppression of polymerisation was observed at much lower concentration then for low molecular weight macromonomers.

The rapid increase of *DP* observed in Figure 3.4. the authors related to the increase in viscosity of polymerisation media with *[M]* due to the macromolecular character of the macromonomer. It is believed that the excluded volume effect can also participate in observed behaviour, especially for the large molecular weight macromonomers, where the molecular weight is large enough to make a random coil approximation. For instance for macromonomer MA-PSt12400 the critical overlapping concentration was estimated in benzene as 1,1*10^{-2} mol/L (by assuming a random coil concentration). However, the rapid increase of *DP* with *[M]* begins at *[M]* = 0,03 mol/L what is three times more then the critical overlapping

concentration of this macromonomer. It should be noted that below this critical value the macromonomers may be prevented from bringing the polymerizable end group close to the propagating radical side by the excluded volume effect or the osmotic effect. On the other side, the sudden decrease of DP at high macromonomer concentrations may be related to the vitrification effect resulting from the glass transition phenomenon [121], in which the segmental diffusion of the end group and translational diffusion of the whole chain are strongly restricted and suppressed. This concentration is related to the polymerisation temperature as well as to the glass transition temperature of the polymerisation system. It should be added that because polymer chain transfer is enhanced by the existence of macromonomers, the effect of the chain transfer reaction on the *DP* of polymacromonomers should also be considered. Such effects were discussed by Hamaide *et al.* during polymerisation of benzyl-terminated PEO in benzene [122].

It can also be seen in Figure 3.4. that the *DP* of polymacromonomers obtained from methacryl-type macromonomers was slightly larger than that of styryl-type at the same *[M]*, although the overall relationship is almost the same irrespective of the type of the polymerizable group. The change of initiator concentration in the range $4{,}2*10^{-3}$-$2{,}56*10^{-2}$ mol/L influenced the molecular weights of the polymacromonomers very slightly.

The plots of conversion versus *[M]* for all studied macromonomers are similar to the one obtained for the dependency of *DP* of polymacromonomers versus *[M]*, as the conversion first increases to some maximum and then decreases to zero in the region where polymerisation is suppressed. It is of interest to note, that conversion began to decrease when the increase of *DP* of polymacromonomers was still continued. This was assigned to the decrease of the polymerisation rate at this concentration and was probably related to the decrease of the initiator efficiency (in each case polymerisation carried out for 24 h).

However, not only homopolymerisation of macromonomers of one type led to the polymacromonomers of high degree of polymerisation, as described by Tsukahara *et al.* Recently, Schmidt et al. [123] described the homopolymerisation of the mixture of two methacryl-type macromonomers of poly(methyl methacrylate) and poly(*2*-vinylpiridine) in benzene with *AIBN* as initiator. Two statistical polymacromonomers of *DP* even higher then described earlier (250 and 650) and of desired compositions were obtained. Nevertheless, the conversion of the macromonomers was below 50 % and for the polymacromonomer of higher molecular weight reached only 26 %.

3.3.2. Homopolymerisation of poly(ethylene oxide) macromonomers in water

However, not always high segment density around the propagating radical limits the polymerisation rate of macromonomers and formation of polymacromonomers of large *DP*. The aggregation or any organization of the macromonomers or the macroradicals during polymerisation were found to have significant influence on these factors [21-24].

The example is the polymerisation of amphiphilic PEO macromonomers in water initiated with *4,4'*-Azobis(*4*-cyanovaleric acid) *(AVA)* reported by Ito *et al.* [21-24, 105]. The high rate of polymerisation, very high *DP*s of polymacromonomers (exceeding 2000) as well as almost quantitive conversion of macromonomer were reported. Additionally, all this three factors appeared parallel so that polymacromonomers of high molecular weights were obtained fast and with high efficiency. The different behaviour of PEO macromonomers during polymerisation in water compared to benzene was assigned to amphiphilic properties of this macromonomer and its ability to self-organization into micellar structure in selective solvent like water (for different parts of the molecule) what will be described below. Under such conditions, the unsaturated groups are concentrated in the micelle, they mostly form the hydrophobic core of aggregates, where hydrophilic shell acts as a monomer reservoir [124-128]. Also the influence of such parameters as molecular weights of macromonomer, incorporation of hydrophobic spacer, or the type of the reactive end group, will be presented.

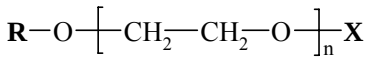
3.3.2.1. Micellization behaviour of amphiphiles based on PEO macromonomers

PEO macromonomers are amphiphilic structures as they consist of hydrophobic and hydrophilic parts. As the result they have all the typical properties of conventional surfactants, such as critical micellar concentration (*CMC*), critical micellization temperature (*CMT*), emulsifying activity, craft point, interfacial tension reduction, etc. [129-131]. The polyether chain is considered as the hydrophilic part, well soluble in water, where all types of ω- and α- end group presented in Scheme 3.13. (except of hydroxyl group) are considered as the water insoluble, hydrophobic groups.

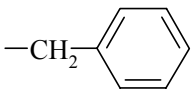
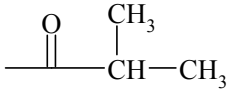
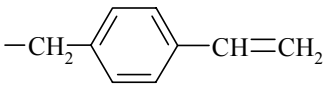
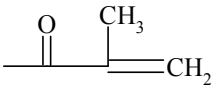
Micelle formation is the result of this amphiphilic nature of the macromonomer molecules. In water the hydrophobic parts try to escape from the aqueous phase and form the *core*, the hydrophilic parts (*shell*) interacts strongly with water molecule. Each micelle consist of a certain number of macromonomer molecules (aggregation number), which determines its size and shape. It was found that in diluted solution, but above *CMC*, micelles are roughly

spherical, but with the increase of concentration the shape starts to change and the deformed spherical, worm-like or disk-like micelles are formed [130]. Additionally, the shape of the micelle depend on the temperature. At low temperature, small spherical micelles are formed. At higher temperatures, the molecular weight of the micelle increases, which can be explained by aggregation of spherical micelles to random clusters. The shape of micelle depends strongly also on the molecular structure of the amphiphilic molecule.

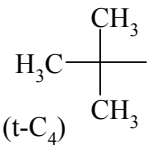
The formation of micelles by PEO macromonomers or their non-polymerizable models of different structure presented in Scheme 3.17 was investigated by Ito *et al.* [20-24, 105] in cooperation of Winnik *et al.* [23] and independently by Liu *et al.* [101].

Type 1  R-PEO-X-n

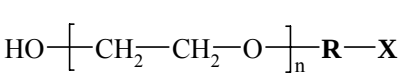
n : degree of polymerization of macromonomer

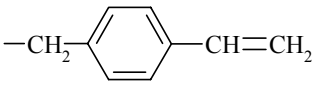
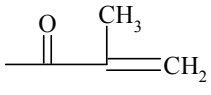
X :  ;  ;  ; 

(Bz) (IB) (VB) (MA)

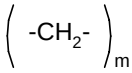
R : HO— ; H_3C— ;  ; CH_3-(CH_2-)$_m$— m = 3, 7,17

(H) (C_1) (t-C_4) (C_4, C_8, C_{18})

Type 2  HO-PEO-R_2-X-n

X :  ; 

(VB) (MA)

R_2 :  (C_1, C_4, C_7) m = 1, 4, 7

X-polymerisable end group or its non-polymerising form

R-end group

R_2 -hydrophobic spacer

Scheme 3.17. The structure of macromonomers and non-polymerizable models of macromonomers used for investigation of micellar behaviour.

Not directly macromonomers, but their non polymerizable models (see Scheme 3.17. type 1) were chosen for the investigations by Ito *et. al.* Instead of vinylbenzyl and methacryloyl PEO macromonomers benzyl and *iso*butyroyl PEO oligomers were studied. The hydrophobic α-group from C_1 to C_{18} was placed at the opposite end of the polyethylene oxide chain. The light scattering was applied as the analytical technique confirming the micelle formation allowing to measure the *CMC* value, root-mean square radius of gyration and molecular weight of micelles.

In case of studies carried out by Winnik *et al*. [23] or Liu *et al.* [101] directly vinylbenzyl- and methacryl-type macromonomers were studied (see Scheme 3.17. type 2). However, this time the hydrophobic spacer of C_1, C_4, C_7, C_{11} and vinylbenzyl- or methacryl- group were placed at the same PEO chain end (polymerizable group separated from the polyethylene oxide with short alkyl chain).

Ito´s investigations of oligomers of type 1 were carried out parallel in two solvents; in water and in benzene. In water, the scattering intensity or the Rayleigh ratio at 90 ° (R_{90}) increased with the concentration above *CMC*, while in benzene negligible scattering was observed, indicating the molecular dissolution of the same polymer. The *CMC* value was dependent on the structure of the investigated polymer and varied from $2{,}6*10^{-5}$ wt-% to $6{,}1*10^{-3}$ wt-%, where the lowest value was obtained for the polymer having C_{18} α- end group. The calculated number of aggregation (m) varied from 20 to 520.

Among all the measured parameters the ratio of the average number of aggregated non polymerizable models of macromonomers in each micelle and the average volume of the micelle appears to parallel closely with the polymerisability of the corresponding macromonomers. This ratio can be a measure of the amount of ω-alkyl groups of the macromonomers in the structure of micelle. Taking into account the obtained results Ito *et al.* proposed the micelle structure of macromonomers as given schematically in Figure 3.5 [21].

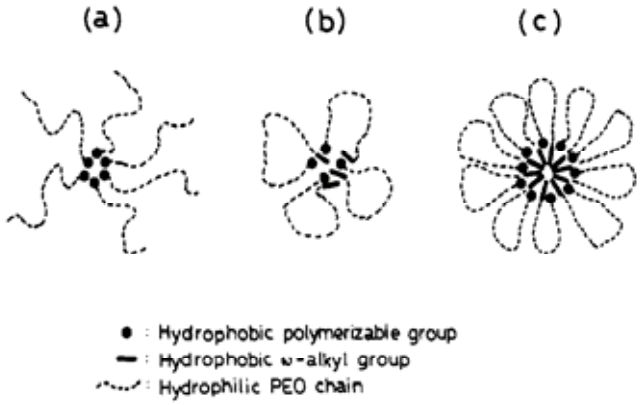


Figure 3.5. Schematic models of micelles of macromonomers with different ω-alkyl groups (a) OH,C_1; (b) C_4, tC_4, C_8; (c) C_8, C_{18}.

Considering the constitution of the macromonomers (or their models), depending from the hydrophobicity of α-alkyl groups the different types of micelles will be formed as is presented in Figure 3.5. In case of C_1-PEO-MA (or VA) and H-PEO-MA (or VA), where at the α end of polymer chain hydrophilic hydroxyl group or slightly hydrophobic methyl group is present the formation into a simple micelle presented in (a) will be privileged. The PEO chains will extend fully into the *shell* to allow a relatively compact arrangement of the hydrophobic α–terminals in the *core* of the micelle. On the other hand, the other macromonomers carrying hydrophobic groups at both ends ($C_m \geq 4$ for initiator group) will organize in another way. The authors reported that the polymers organize into a micelle of a smaller size because the PEO chains are forced to assume loop like (*flower-like* micelles) conformations as in the models (b) for R = C_4, tC_4, and (c) for higher R (C_8 and C_{18}). Model (c) was presented for the highly hydrophobic long alkyl groups, which align themselves very compactly in the *core* with the other, less hydrophobic *p*-vinyl benzyl groups residing at the interphase to the surrounding hydrophilic *shell* composed of PEO chains. It should be also noticed that in case of C_8 loose structure presented in (b) as well as compact structure presented in (c) is possible, so it is believed that in practice the real structure is between the both presented. The same micelles models were later also reported by Maiti *et al.* for acryl type macromonomers [134].

The influence of PEO chain length (*DP* from 13 to 30) on the *CMC* value of compounds of type 1 was investigated and discussed by Ferguson *et al.* [132] and by Maiti *et al.* (*DP* from 8 to 120) [133]. The increase of *CMC* was observed with increasing length of the polymer chain, if only styryl- or methacryloyl- hydrophobic group was present in the macromonomer, while starting from the macromonomer of *DP* = 49 no micellization in water occurred [133]. The

authors assigned the inability to aggregation to the fact that such macromonomers are too hydrophilic to undergo self-organization (the hydrophobicity of end group is significantly suppressed). Additionally, similarly as observed by Ito *et al.* [20-24, 105] the increase of the hydrophobic end group length caused the decrease of the *CMC* value [132].

In case of PEO macromonomers of type 2 (see Scheme 3.17.) studied by Winnik *et al.* [23] as it was expected the lowest values of *CMC* were obtained for the macromonomer with the longest alkyl chain (C_7), confirming that the hydrophobic spacer facilitate the micellization of the polymer chains. However surprisingly, the *CMC* values of this type of macromonomers were above hundred times higher then the one measured by Ito *et al.* using light scattering method and varied from 0,29 to 0,9 wt-%. Additionally, the aggregation numbers of the investigated compounds were much lower then the one obtained by Ito *et al* and did not exceeded 40. To explain that differences they proposed the aggregation model presented below in Figure 3.6.

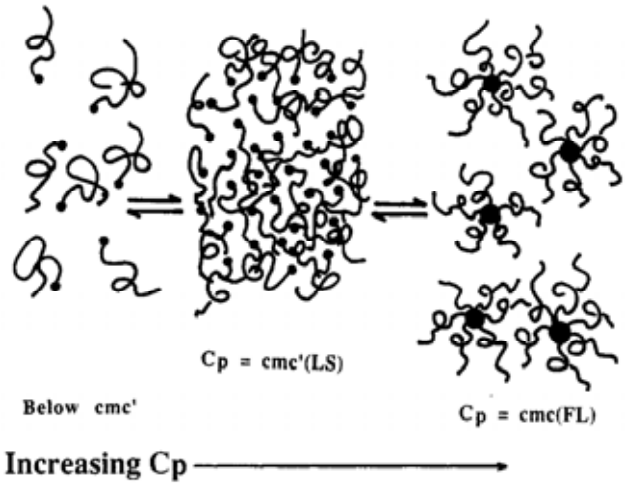


Figure 3.6. The model of micellization in terms of premicelles formation by Winnik *et al.* [23]

They explained this differences in terms of *premicelles* formation. They suggested that the light scattering methods detects any organization of the particles in the solution what not necessary correspond to the formation of well-defined micelles. As presented in the Figure 3.7. at low concentrations the polymer chains do not form any organized forms and only unimolecularly soluble chains are present in the solution. However, above a certain concentration, the polymer molecules associate to form large loose aggregates (*premicelles*), where the hydrocarbon group (black dot in the Figure 3.6.) remain separated from each other. Such moieties are already detected by light scattering method (*LS*) and the concentration is interpreted as the *CMC* at which they are formed. However, the fluorescence probe is not very sensitive to this structures. According to this method the *CMC* values occurs at much higher

concentrations, when the hydrocarbon groups associate to form separate hydrophobic domains, what corresponds to the transition detected by large changes in pyrene fluorescence (soluble in the *core* of the micelle). The *premicelles* theory also explains the differences in the aggregation numbers obtained by this two methods, as much higher amount of chains is involved in premicelle structure (detected by *LS*), then in the well-defined micelle structure (detected by fluorescence probe).

Liu *et al.* [101], who investigated the behaviour of methacryl-type macromonomers of type 2 with alkyl spacer of C_{11} used surface tension method to the determination of *CMC*. He reported the *CMC* value of 0,13 wt-% for the macromonomer of molecular weight 2100 g/mol. His results good correlated with the one obtained by Winnik *et al.* as the increase of the length of the spacer resulted in the decrease of the *CMC* value. Additionally, he proposed the structure of the micelle presented in the Figure 3.8. As it can be seen the organization of double bonds is very dense in the micelle *core*, and even the formation of the loops by the polymer chain with for instance α- end group C_4 should not influence the concentration of reactive groups.

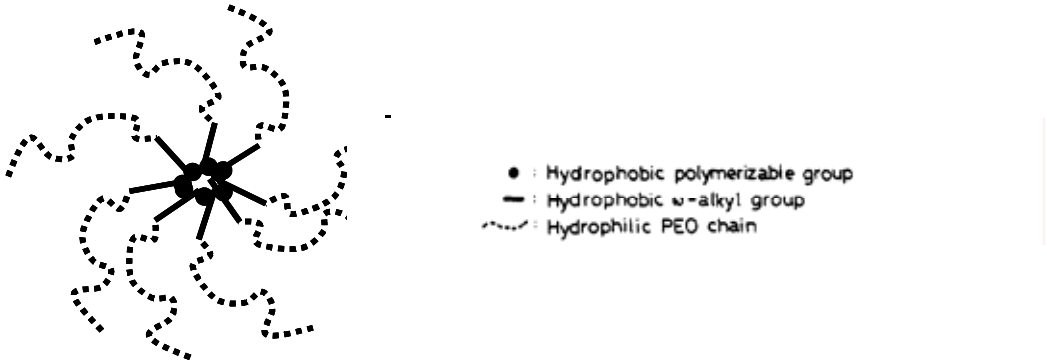


Figure 3.7. Model of the micelle formed by PEO macromonomers carrying the hydrophobic spacer.

3.3.2.2. Rate of polymerisation in water

The rate of the polymerisation of PEO macromonomers in water can be expressed with a conventional relationship in the radical polymerisation as presented in equation 3.10. The mentioned high polymerisability of PEO macromonomers in water appeared to be closely related to their organization into micelles and to the lower rate of diffusion-controlled termination due to their highly crowded segments. The local concentration of reactive group is very high because of the lack of the spatial hindrance.

The studies of R_p of styryl- or methacryl-type PEO macromonomers were carried out by Ito *et al.* [20-24, 105, 135], who calculated the corresponding values from initial slope of the conversion versus time plots for different macromonomers in water. The evaluated values of R_p in water were about two orders of magnitude higher than that in benzene at the same concentration level. Additionally, the rate of polymerisation was decreasing as the conversion of the macromonomer was increasing and at the beginning of the reaction was the highest.

However, although that unusually high R_p was measured an apparently normal kinetic behaviour, described by equation 3.10., was observed. The authors explained that in the context of the micellar polymerisation by considering that k_t may be extremely low and remains constant in the organized micellar environment. Additionally, it is independent of the overall monomer concentration, which is much higher then the critical micelle concentration. As a result the propagation reaction is favoured (increase in k_p). The linear dependence of R_p on macromonomer concentration may simply reflect a linear dependence of the concentration of the micelles, which are the sites of polymerisation, on the overall concentration.

It was found by Ito *et al.* that the nature of the polymerising groups determines directly the chemical reactivity of the macromonomers [24]. Higher rate of polymerisation was observed for the methacrylate PEO macromonomers than for the corresponding vinyl benzyl one. However, the similar observation was made in benzene for PEO macromonomers [136] as well as for conventional monomers such as methyl methacrylate and styrene, so it was rather expected.

More interesting was the influence of presence or lack of hydrophobic alkyl group, its type as well as its location in the polymer chain. Generally, the rate of polymerisation was increasing with increasing hydrophobicity of the α end group (type 1, Scheme 3.17), where for PEO - VB macromonomers the following row was found

$$C_{18} > OH \sim C_8 > C_1 > C_4 > tC_4$$

The highest R_p were obtained for the longest alkyl chain length, however the presence of the quite hydrophilic hydroxyl group at the chain end also highly increased the R_p value. The obtained results were good correlated with the micelle structures presented in Figure 3.5. and Figure 3.7. The higher rate observed in case of polymerisation of PEO macromonomers carrying hydroxyl end group in water was discussed in terms of formation of more compact, denser micelle, giving rise to even higher rate of polymerisation then the corresponding ω

alkyl derivatives. The presence of hydroxyl group increased the hydrophilicity of PEO chains and consequently the stability of micelle. C_4 groups were reported to interact with the reactive end group in the *core* of the micelle causing somewhat looser organization of amphiphilic macromonomers. The existence of the *flower-like* micelles, where the chains take a loop conformation, is entropically disfavoured and makes the barrier between the propagating radical and the unsaturated group. However, the further increase of the hydrophobic chain length caused again the formation of more compact micelle, what again increased the polymerisation rate.

The further increase of the reaction rate was observed if the polymerisation reactive group was separated from the PEO chain with alkyl hydrophobic spacer (type 2, Scheme 3.17), where the longer hydrophobic spacer the higher rate of polymerisation [101]. Such behaviour was assigned to the formation of larger number of more compact micelles (reaction loci), as the presence of spacer favours the association and the grow events. As the result the reactive groups are gathered very close to each other as can be seen in the Figure 3.8., much closer then in case of the macromonomers carrying hydrophobic group at the second end from the reactive group.

The rate of polymerisation increases also with decreasing degree of polymerisation of the macromonomer (from 10 to 60) [21]. As the PEO macromonomers of very low molecular weight are water insoluble and can be polymerised only in benzene the polymerisability of vinyl benzyl PEO macromonomers in water has its maximum for DP = 10 - 25. Such behaviour was attributed to variation in the end group spatial dimension and chain end interactions, because the micelle formation is disfavoured with either too low or too high length of PEO chains [133].

3.3.2.3. Conversion of macromonomers during polymerisation in water

The conversion of PEO macromonomers during polymerisation reaction in water was high and varied from 80 to 100 % for vinyl benzyl type macromonomers [20-24, 105] and from 60 to 100 % for the corresponding methacryl-type ones [137], where in benzene was lower then 50 % [136]. It was noticed by Ito *et al.* that the higher hydrophobicity of the macromonomer alkyl group the higher final conversion can be obtained. In most cases almost quantitive conversion was reached after less then 5 h, where for macromonomers having hydrophobic group of C_{18} even after 30 min. The localization of the hydrophobic group at α- or ω- PEO chain end this

time did not influence the conversion. In the investigated range the length of the PEO chain had influenced the conversion only slightly (*DP* from 20 to 40).

It should be noticed that the enhanced conversion can not be explained by a simple accumulation of the double bonds in micelle causing an increased local reactive group concentration. The linear dependence of R_p on macromonomer concentration meant the independence of the conversion on macromonomer concentration because the conversion, already includes normalization in term of the concentration. However, the enhanced conversion can be explained in terms of increase in the term $k_p/k_t^{0,5}$ in the equation 3.10., because the propagation reaction is favoured in micellar polymerisation, where k_t is very low.

3.3.2.4. Degrees of the polymerisation of polymacromonomers

The degree of the polymerisations of PEO polymacromonomers were much higher than the *DP* obtained during polymerisation in benzene in the similar conditions (concentration, temperature) and for instance, for PEO macromonomers of molecular weight 1000 g/mol exceeded 2000 [20-24, 105, 136]. Ito *et al.* reported that the *DP* of polymacromonomer was dependent from the initial concentration of macromonomer in the polymerisation mixture and was increasing with increasing concentration. Additionally, they observed that the *DP* of polymacromonomer depended on the molecular weight of macromonomer, so that the lower molecular weight of macromonomer the higher *DP* of polymerisation product. They attributed such behaviour to the formation of more compact micelle by the shorter PEO chains, what favours the formation of high molecular weight polymacromonomers. However, the obtained values were much higher (1 to more orders of magnitude) then the degree of aggregation in the micelle of the corresponding macromonomers. This suggested that the micellar polymerisation involved the intermicellar propagation and termination or the reorganization of the micelle during polymerisation [24].

Also high *DP* of polymacromonomers were obtained during polymerisation of methacryl-type macromonomers carrying hydrophobic spacer. The aqueous polymerisation led to the polymacromonomers with *DP* ranging from about 130 to 160, where in benzene the corresponding macromonomers gave the polymers of *DP* 7 [101, 138]. However in contrast to the work described above, the *DP* of polymacromonomers only slightly depended upon the initial concentration of macromonomer in the reaction mixture. Also the length of hydrophobic spacer slightly influenced the molecular weight of the product. The authors

implied that in case of macromonomers carrying hydrophobic spacer the polymerisation proceeded mainly within well-organized micelles with some additional macromonomers from the surrounding area, but no intermicellar interaction was noticed.

3.3.2.5. Influence of the solvent on polymerisation of PEO macromonomers

As it was described the reaction media has an important influence on the polymerisation behaviour of the macromonomers. The polymerisation of PEO macromonomers is very slow in nonpolar solvent (benzene), where days were needed to obtain high conversion of macromonomer. Very fast polymerisation in polar solvent (water) was connected with formation of micelles in water, where in case of benzene, no micellization processes occurred. However, it was found by Ito *et al.* that the polymerisation of PEO macromonomers in cyclohexane, which is also nonpolar, was faster then in benzene, while still much slower then in water [139]. It was also noticed that macromonomers with longer chains polymerised faster in comparison to the shorter one, and to the higher degree of polymerisation. Also, opposite to the polymerisation made in water, the macromonomers with shorter alkyl end groups reacted more rapidly.

To explain this behaviour the authors proposed the model of opposite micelle in which hydrophilic chains are concentrated inside the micelle and hydrophobic reactive styrene groups are placed outside the micelle (Figure 3.8.).

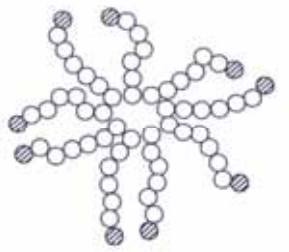


Figure 3.8. Structure of opposite micelle in hexane [139].

When the polymer chains are longer the “mobility” of reactive groups is higher and the polymerizable group can easier get together. It makes the polymerisation easier resulting in the increase of the R_p. The increase of the hydrophobicity of the molecule was assumed to disturbed in the polymerisation by disturbing in the closing of the reactive groups. Nevertheless, such micelles are supposed to be loosely organized and not that stable as those in water and their influence on polymerisation process is not that great as in water. Their

formation favours the polymerisation only to some extent as it was observed. Nevertheless, the obtained results confirmed that any aggregation process have an influence on polymerisation of macromonomers, as they lower the steric screening of the propagation center.

3.3.3. Characterisation and purification of polymacromonomers

As it was presented after the polymerisation of macromonomers usually mixture of the polymerisation product and unreacted macromonomer is obtained. The unreacted macromonomer must be separated from the obtained polymacromonomer or graft copolymer. Two methods are used. If the solubilities of this two compounds differ greatly, then the branched polymer can be purified by reprecipitation. If not the second method is the dialysis of the reaction mixture from the membrane of known molecular weight exclusion limit, higher then the molecular weight of non-functionalized macromonomer, but lower then the mass of graft polymer.

The suitable method used for the characterization of the molecular weights of polymacromonomers as well as their conversion is, similarly as in case of macromonomers, size exclusion chromatography [21-24, 40-45, 114]. The degree of polymerisation of polymacromonomer can be then calculated according to the equation 3.11., as the ratio of average molecular weight of polymacromonomer and the average molecular weight of the macromonomer.

$$\overline{DP}_{polymacromonomer} = \frac{\overline{M}_{n\,polymacromonomer}}{\overline{M}_{n\,macromonomer}} \qquad \textbf{(3.11.)}$$

Initially the molecular weights of polymacromonomers were often measured by *SEC* together with the calibration curve of linear polystyrene standards. As the result, the reported molecular weights of polymacromonomers were smaller then in fact as *SEC* is relative method. Additionally, for such kind of measurements the pure polymacromonomer was required without addition of unreacted macromonomer [20, 47].

For the determination of molecular weight of branched polymers like polymacromonomers, a size exclusion chromatograph, equipped with a laser light scattering detector *(SEC-LS)* in addition to conventional *RI* and *UV* detectors is essential and convenient [113]. Using such

equipment one can rapidly measure the true molecular weight of polymacromonomers and dispersity indices without using isolation procedures to remove unreacted macromonomer.

An example of the plots of molecular weight of polymacromonomers determined by both *SEC* with the linear polystyrene standards and *SEC-LS* with a laser light scattering is presented in Figure 3.9. It is clearly seen that the molecular weights of the polymacromonomers become much larger than the apparent values as *DP* of polymacromonomers increases [113].

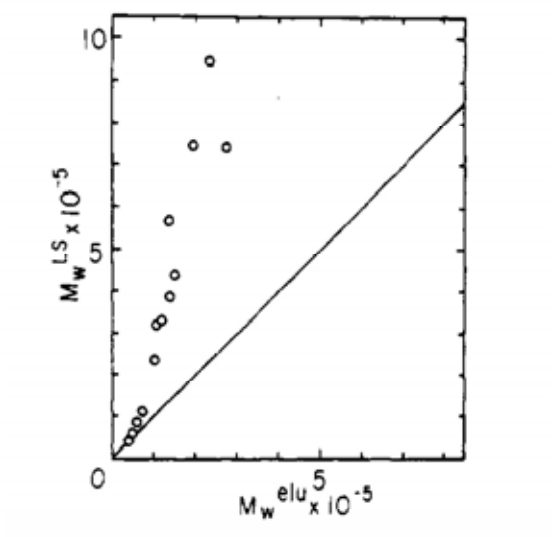


Figure 3.9. The molecular weight determination using *LS* response curve versus the apparent one determined using molecular weight-elution volume calibration curves of linear polystyrene standards [113].

Additionally, it was shown by Ito *et al.* the usual *SEC* calibration based on the linear standard polymers appears to be meaningless for branched polymers [105]. It was found that for a comb polymer (M_n = 1 000 000 g/mol) the usual calibration gave low dispersity index at the level 1,13. However, recalibration using the M_w data obtained from light scattering measurements gave the polydispersity index as high as 3,0-4,9, where similar trends were also true for the other investigated comb polymers.

3.4. Properties of polymacromonomers

3.4.1. Introduction

Homopolymerisation of macromonomers results in branched polymers. Because of the specific regular multibranched structure, they show the following characteristic features as compared with the corresponding linear polymers of the same molecular weight:

- a small and compact molecular dimension;
- a short contour length between any two chains ends along the polymer segments;
- high branch density which affects the conformation of both the branch segments and the chain back bone;
- many chain ends per molecule enhancing the chain end effect (polymacromonomers obtained from polymerisation of vinyl-type macromonomers have polymeric branches on every second carbon atom, what means that one polymacromonomer chain of degree of polymerisation *DP* has *DP+2* end groups).

The size and shape of the polymacromonomers in solution as well as in the solid state relating to the segment density in the molecules depends on the degree of polymerisation of polymacromonomers (Figure 3.10).

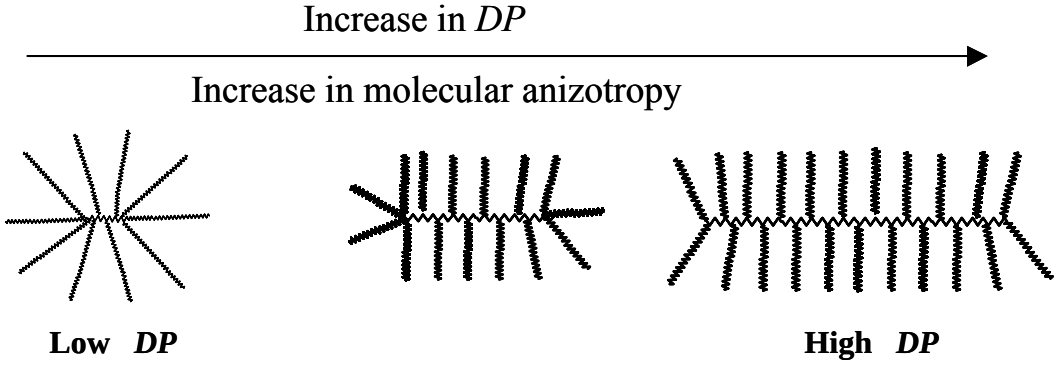


Figure 3.10. Influence of the *DP* on the shape of polymacromonomer.

Generally, polymacromonomers are classified into two types of regular branched forms, i.e. stars and combs, depending on the degree of polymerisation [112]. The polymacromonomers behave as an anisotropic comb-branched polymer when the degree of polymerisation increases to a great extent, while they behave like a star polymers at small *DP* region. When the branch chain length is sufficiently long, the extremely high branch density enhances the

molecular anisotropy; resulting in rod-like molecules, which can induce the formation of the mesomorphic phase. Since both the *DP* of polymacromonomers and the length of branches can be varied they are interesting models for the study of branched polymers [113-115].

As the result of the multibranched structure the bulk properties of polymacromonomers are expected to be significantly different from those of the corresponding linear polymers with similar molecular weight and composition. The polymacromonomers exhibit a variety of characteristics depending upon both the length of the main chain, as well as of the side chains. The molecules with short side chains relative to main chain will behave similarly to the linear polymer, where in the opposite case star-like behaviour is expected. If both side chain and main chain lengths are large the polymer is expected to behave like a comb or brush structure.

3.4.2. Solid state properties of polymacromonomers

Non-linear polymers like stars, dendrimers, or polymacromonomers (brushes) almost always exhibit a clear single glass transition temperature (T_g), however its source is not fully understood. It is believed that in such kind of polymers T_g is rather related to the translational motion of the macromolecules rather then the segmental chain motion [140-142]. In contrast in case of linear polymers T_g is related to cooperative motions of relatively large chain segments and above certain molecular weight the character of the end groups have no influence on glass transition of linear chains, where in case of branched structures the T_g value is strongly influenced by the number and the nature of functional end groups, branching density and the length of the side polymer chains. Other parameters which also have a significant influence on the glass transition temperature of branched polymers are their molecular weights, and the steric effects connected with the crowding and rigidity of the branched structure.

The chain end effect on the glass transition temperature can be described by the relation proposed by Flory *et al.* [143] (equation 3.12.),

$$T_g = T_g^{\infty} - \frac{2T_g^{\infty} v M_0}{v_m M} \qquad \textbf{(3.12.)}$$

where T_g^{∞}, T_g are the values for the polymer of infinite molecular weight, M_0 is the molecular weight of monomer unit, M is the molecular weight of the macromonomer, v_m is the free volume per monomer unit, v is the excess free volume at a chain end. Generally, T_g was found

to increase with increase of the molecular weight of macromonomer (forming side chain) and also that of polymacromonomers [144].

Tsukahara *et al*. studied the properties of poly(styrene) polymacromonomers and revealed that their T_g is predominantly determined by the excess free volume effect of end group per unit molecular weight [144]. The investigated polymacromonomers showed a clear single T_g in *DSC* measurements although they had a small fraction of the methacrylate component as the backbone. Additionally, he reported that in the polymacromonomer structures the molecular cross sectional area, i.e. the effective molecular cross sectional area for entanglements, is very large due to the high segment density around the central backbone segment. Thus, the critical molecular weight for chain entanglements is much greater then those for the linear analogues. As a result a very high degree of polymerisation, or a very short branches are necessary for the entanglements formation in polymacromonomers in bulk.

Additionally, the SAXS measurements of the polymacromonomers in the bulk state made by Tsukahara *et al.* showed that the polymacromonomer molecules exist independently to each other [145]. Such behaviour was confirmed directly by tapping scanning force microscopy [146]. The incompatibility of polymacromonomers was also observed between high molecular weight linear polystyrene and polystyrene polymacromonomers with high degree of polymerisation. However, in spite of the fact they were athermally mixing [147-148].

Branched polymers also have lower melt viscosities and may be processed at lower temperatures compared to linear polymers. The melt viscosity is dependent on the nature of the end groups and for example the increase of the polarity of the terminal groups of hyperbranched polyesters (from propionate to hydroxyl) increases the viscosity of the polymer several times [140].

The lack of entanglements in the structure of polymacromonomers influences their mechanical properties and causes that they are brittle. Tsukahara *et al.* reported that when polystyrene macromonomers are cast onto Teflon or glass plates, many cracks are generally created during the solvent evaporation [144]. The films obtained by such method are too brittle to handle. These features limit the application of branched structures alone in areas where good mechanical properties are needed, however such polymers may be used as additives improving the toughness of other polymers [149-150].

The melting points and the crystallinity were lower compared to those of linear samples. It was attributed to the crystalline imperfections caused by the presence of the branching points and the large number of functional groups. The crystallization behaviour of poly(ethylene oxide) comb-shaped polymers was reported by Wesslen *et al* [151]. The polymacromonomers with the *DP* of side chains lower then 23 were amorphous with T_g in the range of 55-60 °C, where those from side chain *DP* higher then 45 were crystalline with melting point 38-44 °C. Polystyrene polymacromonomers were reported to form lyotropic main chain liquid crystals in the bulk state and in toluene [147-148].

3.4.3. Solution properties of polymacromonomers

The properties of branched polymers are to a great extent influenced by their structure i.e. the higher segment density as compared to polymers of linear structure. The dimensions (the hydrodynamic volumes) occupied by such polymers in solution are smaller in comparison with the linear chains of the same molecular weight, what influence strongly the solution behaviour of branched structures.

A convenient parameter allowing to estimate the contraction of the branched molecule is the dimensionless shrinking factor *g*. It is defined as the ratio of the mean-square radius of gyration of branched polymers $\langle R_g^2 \rangle_b$ and of the mean-square radius of gyration of linear polymer $\langle R_g^2 \rangle_l$ of the same molecular weight (equation 3.13.).

$$g = \frac{\langle R_g^{\,2} \rangle_b}{\langle R_g^{\,2} \rangle_l} \qquad \textbf{(3.13.)}$$

With increase of the *DP* of polymacromonomers *g* value is decreasing.

For the Gaussian chains, the value of *g* for star g_s and comb-shaped g_c is theoretically given as presented in equations 3.14. and 3.15, where *f* is the number of branches and γ is the ratio of the molecular weight of a branch and of the backbone [152].

$$g_s = \frac{3f - 2}{f^2} \qquad \textbf{(3.14.)}$$

$$g_c = \frac{1 + 2f\gamma + \left(2f + f^2\right)\gamma^2 + \left(3f^2 - 2f\right)\gamma^3}{\left(1 + f\gamma\right)^3} \qquad \textbf{(3.15.)}$$

The mentioned *g* factor was determined by Tsukahara *et al.* for polystyrene polymacromonomers with relatively low degree of polymerisation of the backbone [116]. It was noticed that with increase of the excluded volume *g* value was also increasing. That is, the decrease in the molecular size due to the branching is compensated in part by the excluded-effect volume. The obtained results confirmed that polymacromonomers of low degree of polymerisation behave like star polymers. Nevertheless, the experimental values of *g* were larger than the theoretical ones calculated from the equations 3.14. and 3.15. However, taking into account that the measurements were made in good solvent (toluene) where a large excluded-volume effect can be expected.

The obtained results were also confirmed by Gnanou *et al.* who discussed the chain density, radius of gyration, and shrinking factor by means of universal calibration in SEC for comb- and star-shaped polymacromonomers of polystyrene [153] and poly(ethylene oxide) [154-156].

Similar measurements were made by Ito *et al* [157-158] who investigated the dependency of polymacromonomer radius of gyration versus M_w in water and compared with theoretical values. However, in this case the data obtained by both methods were similar. It was found that for the M_w lower then $1*10^5$ g/mol the polymacromonomer acquire a star-shaped conformation and above it the bottlebrush conformation of the polymacromonomer was observed. With M_w higher then $3*10^5$ g/mol the experimental points were fitted by a smooth convex curve. The slope of the convex curve was about 1,54 for M_w between $5*10^5$ g/mol $1*10^6$ g/mol and decreased to 1,15 in the region of M_w between $3*10^6$ and $3*10^7$ g/mol. This change in slope implied that the molecule was rodlike at lower molecular weight region and approached a spherical coil as M_w increased, which is characteristic behaviour of semi-flexible polymers.

Additionally, Ito *et al.* investigated the molecular weight dependence of the limiting viscosity for regular polymacromonomers of poly(ethylene oxide) in THF at 25 °C according to the Mark-Houwink-Sakurada equation 3.16. presented below [105].

$$[\eta] = K \cdot M_w^a \qquad \textbf{(3.16.)}$$

The exponent value *a* depended form the length of the side chains of polymacromonomers and was decreasing with increasing chain length of the branch. For comb polymers with relatively short chains (*DP* = 3; 22) it was varying from 0,6 to 0,7 similarly as for linear PEO and PS, clearly supporting extended coil formation. Each isolated chain in the solution of

these comb polymers apparently behaved like an expanded-coil linear polymer chain, as a whole, although with a much more contracted dimension, as compared to a real linear polymer with the same molecular weight (because of a geometric requirement for the comb structure). For the polymacromonomers with longer side chains (DP = 44; 103) the value of the exponent a was very low or even almost zero. The results suggest a very densely filled, rigid sphere-like conformation, as a whole, for each of these comb polymer chains (zero exponent is required for a rigid sphere). The weak dependence of the viscosity on the molecular weight is very interesting in nature and appears to find applications particularly in the field of paint technology.

Similar results were obtained by Tsukahara *et al.*, who investigated $[\eta]$ of polystyrene polymacromonomer [159]. Additionally, they observed that in high M_w region $[\eta]$ increases and increases with M_w suggesting the change of the conformation of the polymacromonomer from star-like to bottlebrush.

The dilute solution studies on polymer brushes consisting only of polystyrene were reported by Nakamura *et al*. [160-161]. Analysis of the measured R_g based on the worm-like chain with or without excluded volume showed that, while the contour length per chain residue was insensitive to the side chain length, statistical segment length (l_k) under the Θ condition remarkably increased with increasing side chain length. Moreover, they reported that the l_k values for the polystyrene brushes in a good solvent, were about 1,6 times higher then those measured in the Θ solvent. It was concluded that, in addition to the high segment density around main chains, repulsions between the main chain and the side chain and between neighbouring side chains play an important role in the high stiffness of polymer brushes.

Ishuzu *et al*. investigated the dilute solution properties of the alternate copolymer brushes of polystyrene and poly(ethylene oxide) [162]. It was found that these alternate copolymer brushes possessing long aspect ratios form phase-separated cylindrical domains, because incompatible alternating polystyrene and poly(ethylene oxide) side chains align densely on the main chain.

In case of poly(diblock macromonomer)s of polystyrene and polyisoprene or poly(2-vinylpyridine) it was observed that such types poly(diblock macromonomer)s have the advantage of controlling the stiffness of the main chain parts by crosslinking of the inner block of polyisoprene or poly(2-vinylpyridine) [163-164].

Wintermantel *et al*. reported as first that polymacromonomers behave as semi-flexible polymer chains in dilute toluene solution [165-166]. Neglecting the effect of the butyl group (from initiator) and of the ethylene oxide/methacryloyl moieties on the reactive index increment of the polymer, R_g versus the molecular weight relationship of poly(styrene) polymacromonomers was well fitted by a worm-like chain model of the Kuhn statistical segment length. The Kuhn statistical segment length was reported to increase monotonously up to circa 300 nm with branch chain length. They term them molecular bottle brushes. Also small-angle-X-ray scattering (SAXS) experiments supported that results [166].

3.5. Application of macromonomers and branched polymers obtained from macromonomers

One of the most common applications of macromonomers is for emulsion and dispersion systems. The macromonomer technique is unique and simple because the macromonomers themselves plays as emulsifiers or dispersants thus there is no need to add the conventional surfactants. The resulting emulsions or dispersions have a core-shell structure, where the core is formed by the insoluble substrate polymer chains and the shell by the soluble graft-copolymerised macromonomer chains. Thus, such microspheres are sterically stabilized against flocculations [167-168]. Furthermore, the microspheres, more or less monodispersed in size around sub microns to microns, are obtained conveniently in a single step [169-170].

A number of emulsion or dispersion systems in water or in alcoholic media, which are of increasing interest for environmentally friendly systems have been developed using hydrophilic macromonomers. The example are PEO macromonomers, for emulsion or dispersion copolymerisation of styrene and n-butyl methacrylate [171], and polyoxazoline block macromonomers [172] for emulsion copolymerisation with styrene and vinyl acetate.

In addition, various polymeric materials using macromonomers have been already developed, especially in the fields of adhesives, paint and coatings. Usually, macromonomers are used as starting materials for fibres, or as emulsifiers for aqueous or non-aqueous paints [173]. Polyfunctional macromonomers are used as coating materials, adhesives, moldings, or as crosslinking agents in the preparation of different types of gels as well as of microgels [174]. The hydrogels utilizing macromonomers are useful in such application like soft contact lenses and intraocular lenses [173].

The applications of macromonomers include also the synthesis of branch structures such as star polymers, graft polymers, or polymacromonomers by homopolymerisation or by copolymerisation of macromonomers with other low molecular weight monomers [175-176]. The resulting branched polymers may be applied as well in bulk and in solutions or as thin films.

The copolymers of PEO macromonomers with 2-phenyl-2-oxazoline were found to be very efficient surfactants of the non-ionic type, which was assigned to the hydrophilic-lipophilic balance of the copolymers [177]. Increasing the content of poly(ethylene oxide) in the copolymer resulted in improved anti-electrostatic properties.

An interesting area of application of branched polymers is connected with their rheological properties. They are applied as additives, which reduce the melt viscosity of polymers during the processing (for instance addition of hyperbranched polyphenylenes reduce the viscosity of melted poly(styrene) considerably) [149].

Another application of graft copolymers is surface active polymeric additives for the surface modification of polymeric materials, what is very important in such field as biomaterials, chromatography, coating, adhesives, antistatic properties and many others. Surface modification utilizing the surface adsorption or surface accumulation of the additives having desirable properties, like antistatic and antioxidative properties, has been very popular and used for a long period [173]. Branched polymers were also used as compatiblizers in polymer blends and alloys as kind of interfacial modifiers [173].

Copolymers synthesised from amphiphilic macromonomers might find a number of promising applications. The core-shell cylindrical molecules can be used for preparing nanoscoping channels, wormlike micelles, and other complex architectures [173]. The copolymers of PEO macromonomers with styrene and maleic anhydrate gave polymers where by changing the structure, composition and nature of the functional groups it was possible to obtain products with the desired degree of water uptake [178]. These copolymers are potential non-aqueous surfactants since they form stable emulsions in water-methanol, heptane, hexane and ether. Depending on their structure and composition it was possible to obtain surfaces with contact angle from 68 ° to complete wetting by water.

The application of branched polymers in solid-state batteries and ion-conducting membranes is possible. It was found that comb like amphiphilies with PEO side chains on styrene-maleic anhydride or ethylene-maleic anhydride copolymers converted to their lithium salts showed single-ion conductivities [179]. Additionally, polymers based on poly(ethylene oxide) macromonomers bearing sulfonate groups displayed single-ion conductivities and other properties suitable for use as solid electrolytes in batteries [180].

The correlation between the structure and the dispersing activity in coal-water mixtures of non-ionic comb-like copolymers investigated for poly(4-methoxystyrene)-g-poly(ethylene oxide)s showed the possible application of these copolymers as dispersants in coal-water mixtures [181].

A very interesting feature of some grafted copolymers is their ability to form physical gels due to a strong interaction and aggregation of the polyether grafts [182-183] (for instance the polyacrylamide copolymers with poly(ethylene oxide) grafts). This kind of molecular organization in selective solvents which leads to enhanced viscosity or the formation of monodisperse hydrogel microspheres is expected to find various applications as shear-thickening agents, toughening agents for surface coatings and adhesives, and various uses in the field of biology, medicine and pharmacology [183-185].

3.6. Applied polymerisation techniques

One of the main goals in modern synthetic polymer chemistry is to prepare polymers with predictable, well-defined molecular weights and with desired architecture. A polymerisation process is based on a repetitive reaction in which a monomer is converted into a polymer segment. To achieve such a goal there exist a variety of synthetic processes to choose from. Nevertheless, each method has its strengths and weaknesses. Therefore, many factors has to be taken into account before starting the synthesis.

Radical polymerisation is the most important process leading to high molecular weight polymers [186]. However, despite of simplicity and low costs, the significant drawback of conventional radical polymerisation is related to the lack of control over macromolecular structure of products. The synthesis of block copolymers is practically impossible via the sequential addition of monomers, which leads to a mixture of homopolymers (no living radicals at the end of each monomer addition step and new need to be produced to start the polymerisation of the new monomer).

On the other hand, ionic polymerisations i.e. anionic or cationic are suitable for a controlled growth of polymer chains since these reactions proceed one step at a time and can be stopped at each step if desired [187-190]. The control over molecular weight, molecular weight distribution as well as the structure of synthesised products (block polymers) is thus very good. However, the demanding conditions (high purity of monomers, exclusion of oxygen and moisture) and requirements of highly sophisticated equipment made these techniques difficult.

More recently, new group of controlled polymerisations commonly known as controlled radical polymerisation *(CRP)* [191-194] was developed. The main concept of this technique includes the decrease of the concentration of the growing radicals resulting in the decrease of the contribution of termination reactions. A few techniques differing with the way of diminishing of the radical concentration was developed in the past few years, including atom transfer radical polymerisation (*ATRP*), nitroxy mediated radical polymerisation (*NMRP*), or reversible addition-fragmentation reaction (*RAFT*). Generally, all these techniques allow to prepare polymers of well-defined structure, but since they are based on radical active sites, are more tolerant to impurities and larger monomer variety, including macromonomers can be polymerised in controlled way [195].

Thus, different polymerisation techniques were used for the preparation of macromonomers and polymacromonomers. As well-defined narrow distributed macromonomers, with controlled chain length were desired anionic living polymerisation was used for their preparation. In contrast, preparation of polymacromonomers included radical polymerisation of macromonomers, where both conventional radical and controlled radical methods (*ATRP*) were used. The principles of the applied polymerisation techniques are described below.

3.6.1. Anionic living polymerisation

Among living polymerisation techniques, one of the most effective methods for the precise polymer synthesis seems to be the anionic living polymerisation. The concept of carbanions as an initiating moiety has been considered in 1940's [196], however the first fully characterized example of living anionic polymerisation was reported by Szwarc in 1956 [197]. Nowadays, despite of continuing development of new strategies of well-defined polymers and copolymers (e.g. group transfer polymerisation, controlled radical polymerisation etc.), anionic polymerisation continues to be the most reliable and versatile method for the synthesis of a wide range of polymers. [187-190].

3.6.1.1. Fundamentals

Szwarc proposed the term *living polymers* for those macromolecules which may spontaneously resume their growth whenever fresh monomer is supplied to the system. [197]. Thus, all active centres generated upon initiation step remain active and the polymer chains grow until all monomers are consumed, and resume their linear grown, whenever fresh portion of monomer is added to the system. However, two conditions has to be fulfilled so that such behaviour could be observed. First, no side reactions such as termination or chain transfer can appear in the system. Secondly, the rate of initiation of the polymerisation has to be fast or at least comparable to the rate of propagation. Under such conditions all initiator molecules initiate simultaneously polymerisation, and all chains start growing at the same time.

However in practice, side reactions are unavoidable and can't be completely suppressed. Traces of water, oxygen, carbon dioxide and other impurities introduced to the polymerisation system with monomer, solvent or initiator cause the termination of the chain and the broadening of the molecular weight distribution of polymers. Therefore, their amount should be rigorously decreased, what makes anionic polymerisation a very demanding technique

(ultra purity of reagents and solvents, high vacuum etc), somewhat limiting applicability of anionically initiated polymerisations. In practice the term *living* is applied referred to polymerisation systems, in which the rates of side reactions of termination caused by presence of impurities are sufficiently slow to permit successful completion of a desired task. Under such conditions the polymers with controlled molecular weights and narrow molecular weight distributions can be obtained.

Since in *living* system initiation is quantitative, tailoring of the molecular weight of products is based on the variation of amount of added initiator. Since side reaction are suppressed, all molecules are allowed to grow under the same conditions, the degree of polymerisation (DP_n) of the product formed by this technique is given as the ratio of the total number of added monomer $[M]_0$ to the total number of active centres. Taking into account the quantitative initiation (i.e. one living polymer chain per initiator molecule), the total number of active centers corresponds to concentration of initiator $[I]_0$ and at full conversion of the monomer the DP_n of the product can be then described as presented in equation 3.17.

$$\overline{DP_n} = \frac{[M]_0}{[I]_0} \qquad \textbf{(3.17.)}$$

DP_n – degree of polymerisation of the polymer
$[I]_0$ – concentration of initiator
$[M]_0$ – the initial amount of added monomer

The degree of polymerisation of polymer obtained by anionic polymerisation increases linearly with conversion since all macromolecules grow proportionally to the amount of monomer consumed. At given period of time *DP* of the product can be thus calculated according to the equation 3.18.

$$\overline{DP_n} = \frac{[M]_0 - [M]_t}{[I]_0} \qquad \textbf{(3.18.)}$$

Other common criteria used for polymer characterization is dispersity index (M_w/M_n), which refers to the unity of polymer chains length in the sample. For living polymerisations with fast initiation, the molecular weight distribution calculated according to the equation 3.19. is identical with the *Poisson distribution function* and do not exceed 1,1.

$$\frac{\overline{M}_w}{\overline{M}_n} = \left(\frac{\overline{DP}_w}{\overline{DP}_n}\right) = 1 + \left[\frac{\overline{DP}_n}{\left(\overline{DP}_n + 1\right)^2}\right] \qquad \textbf{(3.19.)}$$

M_w – number average molecular weight

M_n – weight average molecular weight

3.6.1.2. Mechanism of anionic living polymerisation

General aspects of polymerisation mechanism have been discussed and described in details in several reviews [187-190]. The centers of growth in anionic polymerisation are carboanions (the case of vinyl compound), while in the polymerisation of heterocycles the negative charge is usually located on heteroatoms.

Generally, anionic polymerisation as a conversion of monomer by nucleophilic center to monomeric segment of the polymer chain can be described by equations in Figure 3.11. [198].

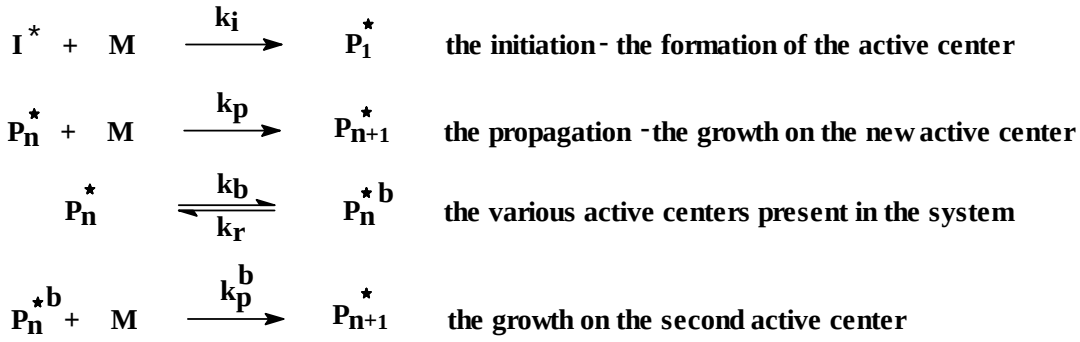


Figure 3.11. Kinetic of anionic *living* polymerisation.

In the initiation step molecules of initiator with marked nucleophilic character reacts with the monomer whose electrophilic character is low and the growing chain bearing an anion or negative polarization is formed. The negative charge of the polymerising chain is neutralized by the corresponding counterion. As no side reaction is present in the system the growth of the chain is continued until the whole available monomer is reacted. The next step can be addition of a second monomer (block copolymer formation) or the active end group of living polymer may be annihilated by suitable electrophile to generate desired functionality [33-56]. As example, mentioned macromonomers formation can be given.

Since the oppositely charged cation and growing macroanion of polymer chain attract to each other and strongly interact with polymerisation medium, variety of species may coexist in

polymerisation systems. Generally, the initiating species obtained by the solubilization of initiator can be divided into few solvation forms like: *tight (contact) ion pair, loose ion pair* and *dissociated ions* [187-190]. All of them coexist in the polymerisation system in equilibrium and each type of active end group propagates according to its kinetic constant of propagation. The reactivity towards monomer is mainly affected by the distance between anionically growing centre and counterion and can be put in a row: *tight (contact) ion pair* ≤ *loose ion pair* << *free ions*. Thus, in order to have the same conditions for all growing chains and to keep the control, exchange between active species must be fast, or at least faster then propagation rate.

The position of solvating equilibrium may be influenced by such parameters as the sort of solvent and counter anion as well as by temperature. The influence of the solvent is complex. Generally, polar solvents with high dielectric constant are likely to induce ionisation as well as the dissociation of *ion pairs* into the most reactive *free ions*. Also solvating power of the solvent is of great importance where solvents possessing high solvating power lower the cation-anion interactions energy and more reactive separated ion pairs are formed. Special class of solvents with high solvating power are so-called crown ethers, crown amines or cryptands, which cavity is exactly adjusted to the ionic radius of the cation, which is complexed. The addition of such compound, considerable improve the formation of free ions.

The nature of counterion also affects the solvation equilibrium. In most cases alkali metals or alkaline-earth metals are introduced as counterions. Because larger ions separate easier from the growing macroanion and form more active free ion centers the reactivity of polymer chain increases with increasing size of the alkali counterion, i.e. from lithium (Li^+) to cesium (Cs^+).

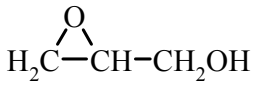
Also temperature influences the dissociation equilibrium of ion pairs to free ions. The concentration of free ion active centers increases with the decrease of the temperature. Thus, the higher propagation rates of the reaction may be expected at lower temperatures.

3.6.1.3. Anionic polymerisation of oxiranes

Extensive studies of the mechanism and kinetics of the anionic polymerisation of oxiranes have been summarized in several reviews [189, 199-200]. The high negative enthalpy of polymerisation of this kind of monomers originates from the strain in the oxygen ring, making them suitable for ionic polymerisation [201].

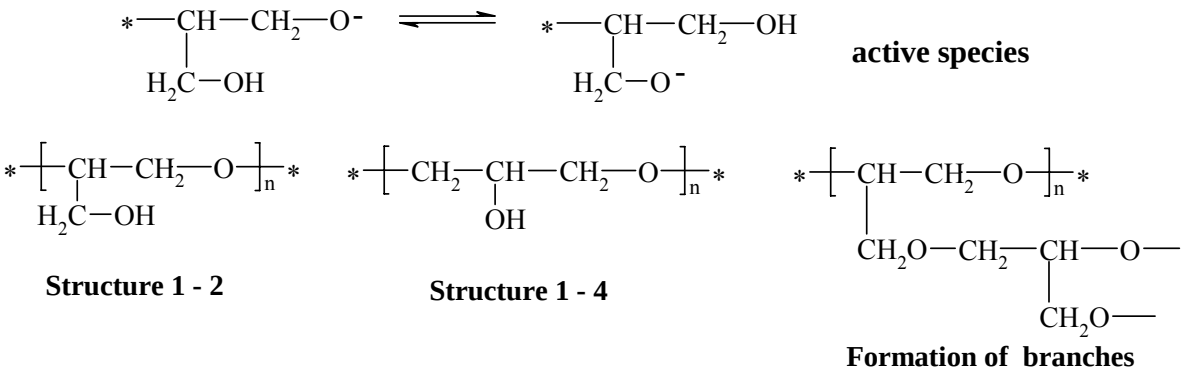
The most studied oxirane monomer is ethylene oxide. The earliest works led to polymers with relatively low molecular weights as the result of the chain-transfer reactions [202-203]. The investigators added alcohol to the polymerising solutions to solubilize the insoluble in the reaction media alkoxides, which caused the formation of new initiating forms in the polymerising system. As first Worsfold *et al.* [204] reached *living* character of the reaction using sodium and potassium salts of mono-methyl ether of diglyme, $CH_3OC_2H_4OC_2H_4O^-$ as the initiators and carrying out polymerisation in aprotic media (hexamethyl phosphoric triamide). Additionally, several papers have been published on the anionic polymerisation of ethylene oxide in DMSO initiated by metal alkoxides, where also good control of the reaction was observed [205-207]. Kinetics of polymerisation of ethylene oxide in ethers (THF) was also reported [208]. However, the polymerisation in those system was not effective what was caused by the association of the polyalkoxides followed by extremely low dissociation constant of alkoxide ions pairs. In further works the association of polyalkoxides in THF was avoided by complexing the cation with suitable cryptands [208-209]. Under such conditions, where negligible association was observed, the polymerisation system showed the features of anionic living polymerisation.

The other widely studied oxirane monomer is glycidol presented in Scheme 3.18., which can be considered as analogue of ethylene oxide, where one hydrogen atom was replaced with hydroxymethyl group.



Scheme 3.18. Glycidol structure.

As glycidol is a bifunctional monomer upon polymerisation the simultaneous presence of epoxy and hydroxyl groups in the structure causes transitions of the alkoxide active side from primary to secondary, as well as, intramolecular chain transfers as presented in the Scheme 3.19 [210-211]. This exchange equilibrium between inactive hydroxyl and active alkoxide end groups is intrinsic for this process, thus leading to multiplication of active centers. As the result the direct polymerisation of glycidol leads to brunched structures.



Scheme 3.19. Multiplication of active centers and possible structures upon polymerisation of glycidol.

Glycidol was first polymerised by Sandler *et al.* [212] using different initiators (hydroxides: potassium, sodium, lithium or amines: pyridine, triethylamine), who concluded that in comparison to propylene oxide, glycidol is more reactive. Since that time glycidol was polymerised in different ways, where both cationic [27, 213] and anionic synthesis routs [214] were reported. Additionally, Frey *et al*. carried out anionic polymerisation of glycidol with slow monomer addition to get the poly(glycidol)s with very high branching density [214].

The preparation of linear poly(glycidol)s is also possible. However, to attain this goal the selective, reversible protection of hydroxyl group of the monomer is necessary. The choice of the protective group has to be made taking into account two things: the protective group should be stable under polymerisation conditions (high reactivity of macroanion), and be removable selectively and completely under conditions, where cleavage or decomposition of the polymer structure is not observed.

The first protected glycidol was obtained and polymerised by Vanderberg *et al*., who reversibly blocked hydroxyl group by etherification and sililation [210].

The other kind of protected group was proposed by Spassky *et al.* [211], who introduced 1-ethoxy ethyl group upon reaction of glycidol with ethyl vinyl ether [216]. The obtained 1-ethoxy ethyl glycidyl ether for simplicity called glycidol acetal is stable in basic media, however in acidic conditions the protective group could be removed. Additionally, upon anionic polymerisation no side reaction or intramolecular chain transfer was observed and linear, narrow distributed poly(glycidol acetal)s, with controlled molecular weights in good agreement with targeted one, were obtained.

3.6.2. Radical polymerisations

As it was mentioned in comparison to the living anionic polymerisation processes based on radicals are much easier to perform. They are more tolerant to the presence of impurities, or different functionalities in the monomer structure and can be carried out in the presence of water within a convenient temperature range. However, the main requirement of such type of polymerisation is the lack of oxygen, which presence leads to deactivation of radicals [195].

3.6.2.1. Conventional radical polymerisation

The scheme of radical polymerisation is presented below in Figure 3.12.

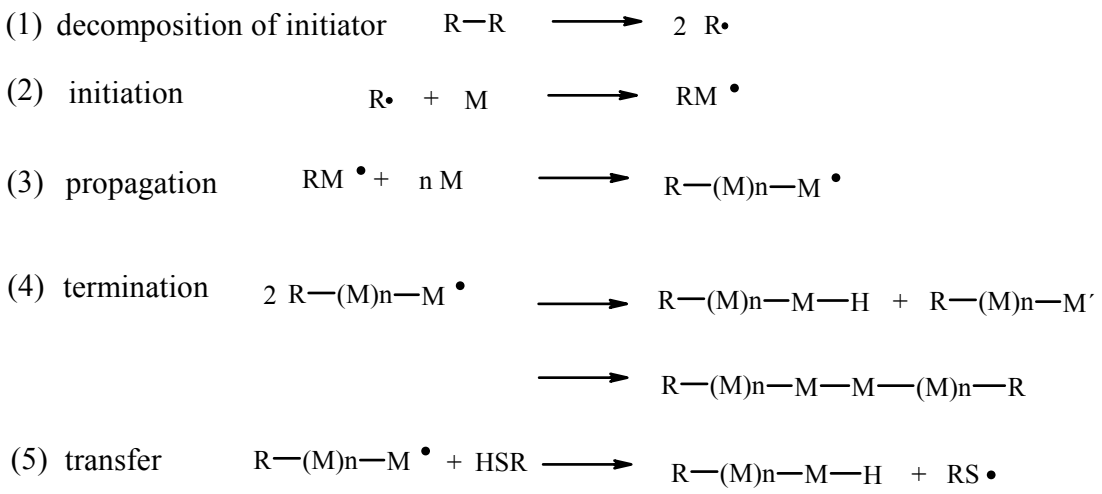


Figure 3.12. Kinetic of conventional radical polymerisation.

The five processes of importance in vinyl polymerisation by radical mechanisms are: (1) decomposition of initiator; (2) initiation of the polymerisation; (3) propagation (the successive additions of monomer to the radical); (4) termination by reaction of two radicals to produce inactive polymer or by disproportionation; (5) transfer (the termination of one polymer chain and initiation of a new polymer chain).

Polymerisation systems that involve propagating radicals involve very short-lived intermediates. Under such conditions termination reactions are very fast, being diffusion controlled [217]. The formed radicals exhibit a pronounced inclination to recombine or disproportionate, what is in contrast to cationic or anionic chain ends in ionic polymerisations, as they do not react with one another because of static repulsions. Indeed, radicals recombine and/or disproportionate with rate constants approaching the diffusion-controlled limit; i.e. $k_t \sim$

$10^{8 \pm 1}$ $(mol*s)^{-1}$, which is much higher than the corresponding propagating rate constant, $k_p \sim 10^{3 \pm 1}$ $(mol*s)^{-1}$. Moreover, the initiation is usually incomplete due to slow decomposition of classic radical initiators; i.e., $k_d \sim 10^{-5 \pm 1}$ s^{-1}. As the result radicals are generated form initiators and initiate the growth of new polymer chains as the propagation step already proceeds.

The most important chain-breaking reaction in radical systems is the termination between two growing radicals [218]. Normally, all processes presented in the Figure 3.12. proceeds at once and the molecular weight of the resulting polymers is determined statistically by the competition of process (3) with processes (4) and (5). These are the kinetic reasons why classic radical polymerisation process yield ill-defined polymers with uncontrolled molecular weight. Additionally, the resulting polymers exhibit generally quite broad molecular weight distribution. Theoretical calculation suggests that the lowest polydispersity that could be achieved by a conventional radical polymerisation process is at least 1,5 [219]. However, in most cases polydispersities close to 2-3 are obtained for poly(vinyl monomers) synthesized on a small or an industrial scale [195]. For radical synthesis of copolymers, the polydispersities are generally much higher, what mainly precludes the preparation of polymers with complex architectures. Moreover, the properties of the polymers produced in the polymerisation reaction can be adversely affected by a high incidence of initiator or chain transfer fragments residing on the polymer chains.

3.6.2.2. Atom transfer radical polymerisation (*ATRP*)

The basic idea of *CRP* polymerisations involves a drastic reduction of the concentration of the momentarily present radicals, which is achieved by creating conditions enabling fast exchange between them and the corresponding dormant species. In an ideal case, these polymerisations proceed in the absence of side reaction i.e. chain transfer or termination processes, however in real systems termination occur, mainly through radical coupling or disproportionation. However, its contribution of the polymerisation is small (no more than a few percent), without significant influence on final polymer properties. Thus, the term controlled is usually used to describe free-radical polymerisation systems in which molecular weights and dispersity indices may be controlled, although they are not terminationless [195].

Among various *CRP*-type polymerisations, metal catalysed atom transfer radical polymerisation (*ATRP*) has attracted a great attention. The reduction of concentration of

radicals in *ATRP* is based on the transfer of an atom (usually a halogen) from a dormant initiator or polymeric chain to a transition metal salt, catalysed by ligated salt. The general mechanism of this type of polymerisation is depicted in Figure 3.13.

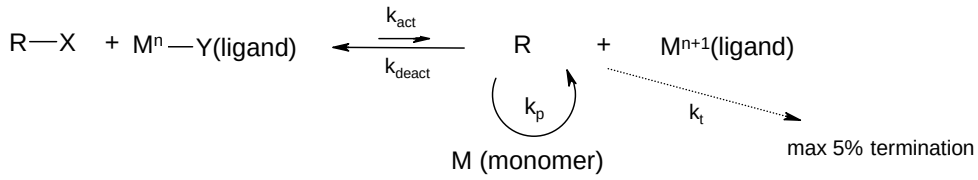


Figure 3.13. Scheme of transition metal catalysed polymerisation (*ATRP)*.

During atom transfer radical polymerisation formation of radical is based on reversible redox process catalysed by a transition metal complex depicted as M_t^n –Y. It undergoes an one electron oxidation M_t^{n+1}–Y with simultaneous abstraction of a halogen atom X. Initiation of the polymerisation reaction is then accomplished through homolytic cleavage of halogen containing compound and the addition of generated radicals to the monomer. Thus, at initiation step, initiator (R–X) reacts with the catalyst system M_t^n –Y/L forming radical and oxidized metal catalyst system. The formed radical $R^\bullet$ adds in the following steps to the monomer to generate the polymer radical species $P_1^\bullet$ and propagation of the polymer chain proceeds. Upon growing the polymer chain is reversibly deactivated to the dormant species (P_1–X) many times via abstraction of halogen atom from X - M_t^{n+1} –Y/L complex and activated by the homolytic cleavage of terminal chalogen-carbon bond, what promotes many polymerisation cycles.

In order to control the growth of the polymer chain the atom transfer equilibrium constant of activation-deactivation reactions must be strongly shifted in favour of the dormant species and the exchange between the two forms dormant and active must be very fast. Additionally, equilibrium must be established fast at the beginning of the polymerisation, what means that the initiation must be fast and quantitative as active species must be immediately deactivated. Moreover, deactivation-activation process of the active species must be faster as the propagation, to provide the same possibility of growth to all polymer chains. If the mentioned conditions are fulfilled, the momentary concentration of radicals in the polymerisation system is very low and their life time very short.

This strategy permits to drastically reduce the probability of collisions between radicals and undesired side reactions. However, as termination by recombination of growing polymer

chains can not be entirely avoided in these systems the dispersity indices of polymers prepared by these techniques are not as narrow as those prepared by living anionic polymerisations. Nevertheless, according to assumed mechanism concentration of active species should remain constant during whole polymerisation process resulting in linear increase of $ln([M]/[M_0])$ and the molecular weight of the polymer in time. The degree of polymerisation of obtained polymers can be predominated thus by the ratio of consumed monomer to the initiator $DP_n = \Delta [M]/[I_0]$.

- ***ATRP* polymerisation system**

As it was presented the *ATRP* process is always carried out in multicomponent systems. Control over final polymer properties strongly depends on the proper choice of the polymerisation system i.e. initiator, transferable halide atom, transition metal, ligand, solvent, deactivator, or temperature. The influence of different components is shortly described below.

Catalytic system

The most important component in the *ATRP* polymerisation systems seems to be the applied catalytic system i.e. complex of employed transition metal halide with the ligand, as it generates radicals upon deactivation-activation processes and determines the position of equilibrium between dormant and active species of the growing polymer chain. There are several prerequisites for the efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation.

The most common studied class in terms of versatility and costs are copper-based catalyst systems, however other metals like ruthenium, iron, nickel were also employed [191].

Ligands should complex the metal relatively strongly as their main role is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer [220]. Although there are no consistent rules for the design of catalyst systems, it was found that the electronic and steric effect of the ligands influence its properties significantly. Reduced catalytic activity or efficiency was observed when excessive steric hindrance around the metal centre was obtained or ligand with strongly electron-withdrawing substituents was used [221]. As the

result among a variety of used ligands nitrogen-based one have been used most commonly for copper-mediated *ATRP*. It was found [222] that the activity of *N*-based ligands decreases with number of coordinating sites (N4>N3>N2>>N1) and with the number of carbons between atoms of nitrogen (C2>C3>>C4). Additionally, the activity of ligand is also influenced by its topology, and is usually higher for bridged, or cyclic form than for their linear analogues. Some examples are presented in Figure 3.14.

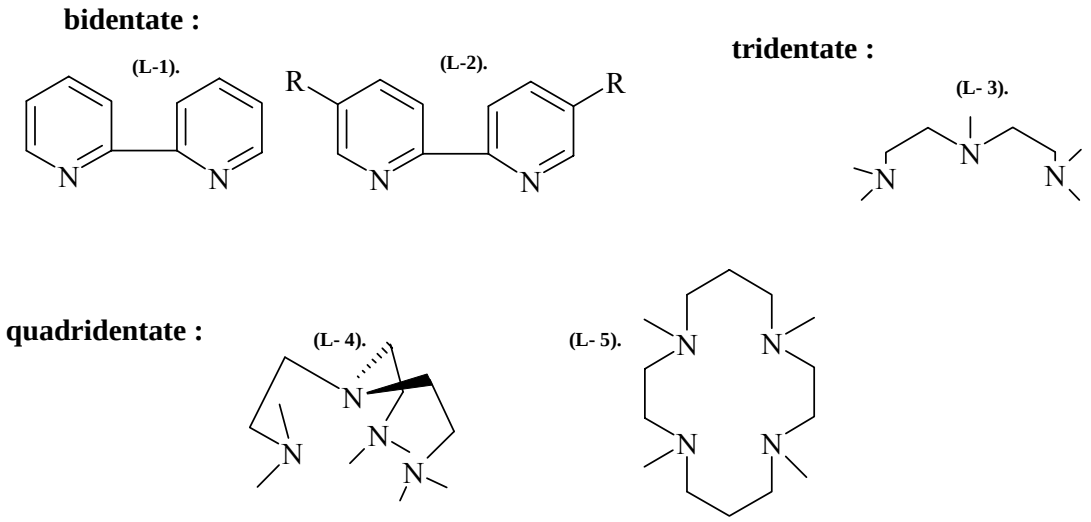


Figure 3.14. Example ligands for copper-based catalysts; **L-1** *2,2'*bipyridine (bpy); **L-2** substituted *2,2'*bipyridines i.e. *4,4'*-di(5-nonyl)-*2,2'*bipyridine (dNbpy), *4,4'*-di-*t*-butyl-*2,2'*-bipyridine (dTbpy); **L-3** *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA); **L-4** tris[*2*-(dimethylamino)ethyl]amine (*Me_6TREN*); **L-5** *1,4,8,11*-tertramethyl-*1,4,8,11*-tetraazacyclotertradecane (*Me_4Cyclam*).

Initiators

In controlled processes, the main role of the initiator is determination of the number of growing polymer chains. There are few general considerations for the initiator choice: (1) its structure should be similar to the structure of the growing chain end; (2) the reactivity of initiator should be comparable of the subsequently formed growing chains; (3) the dissociation of the halogen-carbon bond should be fast (bond strength Cl > Br); (4) halide atom must rapidly and selectively migrate between the growing chain and the transition metal complex. α-substituted alkyl halides both chlorine and bromine were found to fulfil this features and as the result are commonly used as the initiators in *ATRP* systems [223].

Solvents

ATRP can be carried out in bulk, in solution or even in a heterogeneous system (e.g., emulsion, suspension), however, the most commonly applied are solution-based systems. The great variety of solvents was used in *ATRP* polymerisation, however such factors as a chain transfer to solvent, catalyst poising by the solvent [224] or solvent-assigned side reaction such as elimination of HX from initiator moiety [225] should be minimized in the applied polymerisation system. Additionally, the possibility that the structure of the catalyst may change in different solvents should also be taken into consideration [191]. Yet, the addition of solvent usually improve solubility of catalytic systems [191, 195, 226] and is inevitable, especially when obtained polymer is insoluble in its monomer. The dilution of the polymerisation system decrease the concentration of radicals, what decrease the probability of their collision and of termination reactions. Sometimes also the increase of the polymerisation rate in presence of polar medium like water was observed [227-228].

Temperature and additives

Temperature influences both the rate of the polymerisation as well as the atom transfer equilibrium constant. Thus, at elevated temperatures but lower then the catalyst decomposition temperature [191] better control of the chain-growth should be obtained. However, the increase of the temperature results in the increase of the rate of side reactions. Thus, the optimal *ATRP* temperature depends on the polymerisation system and is the compromise between mentioned factors.

Additives are sometimes essential for a successful *ATRP*. The rate of the reaction may be changed by addition of accelerators or deactivators to the polymerisation system, depending on which effect is desired. For instance, it was found that introduction of small amount of copper (0) upon polymerisation of styrene, resulted in significant increase in polymerisation rate, where well-defined polymers were obtained [229]. Moreover, if sufficient amount of zero covalent metal was present in the system, the *ATRP* was carried out without removal of oxygen or inhibitor [230]. In contrary, if a small amount (≈ 10mol%-) of the deactivator such as copper (II) was added to the polymerisation mixture, suppression of propagation rate was observed [231].

4. Analytical methods

In this section the most important techniques used for characterization of macromonomers and polymacromonomers will be described.

4.1. Size Exclusion Chromatography (*SEC*)

Size exclusion chromatography is a standard method for polymer characterization [232]. The advantages of that technique over the other separation methods are the small amounts of substances used to analysis, relatively short separation times and highly automated equipment. A characteristic feature of this separation method is the independence from test conditions such as temperature, pressure and to some extent from solvent, load and flow rate.

SEC is a specific form of liquid chromatography. It is based on separation of dissolved polydispersed macromolecules using porous media into monodispersed fractions of different molecular weights. During such measurements the choice of the solvent plays a crucial role as the substance-specific interactions between stationary phase and substance can not occur and the solvent can not react with the solute or the gel. Moreover, the eluting agent influences the separation efficiency via a diffusion coefficient, where for low eluent viscosities, the number of theoretical separation stages increases. Finally, the solvent must be compatible with the detector.

Compared to other chromatography methods *SEC* can be characterised by the following properties:

- separation is effected according to the volume of the polymer in the solution;
- larger particles are eluted before smaller ones;
- separation takes place in a volume that is smaller than the total volume of the column.

As the result the concentration of the stationary phase is never larger than that in the mobile phase and the stationary phase has the same composition as the mobile phase, but differs in its lack of mobility.

The accessibility of the pores by diffusion to different molecules is a function of both molecular and pore size. The smaller the molecules, the deeper they penetrate into the pores of the gel. Smaller molecules are therefore eluted only after larger molecules. Molecules whose average hydrodynamic radius is larger than that of the gel pores cannot be separated.

Since at any point not all molecules diffuse into the available pores, a zone broadening of the elution curve occurs. As the result this effect interferes with the separation of narrowly distributed products and requires correction, while for very broad distributions can be neglected. Moreover, the so-called skewing effect arising from the change in the elution volume due to the amount of the sample added to the column must also be taken into account. In thermodynamically ideal solvents shifts of the elution volume are measured as a function of sample concentration. This effect increases as the molecular weight increases.

Generally, *SEC* systems consist of the separation columns, a non-pulsating pressure pump with adjustable flow rate, a sample injector valve with a sample volume loop and a detector. Usually, RI and UV filter detectors are used. Upon measurements, a sample volume loop is filled using a sample injector syringe.

SEC is a relative method as it measures the volume of the polymers but not directly their molecular weights. Non of the proposed theories allows the derivation of the precise correlation between elution volume and the molecular size. Therefore each separating column must be calibrated with polymer standards of known molecular weight. When the solvent is changed the column must be recalibrated. Experiments gives an elution chromatogram which is converted into the molecular weight distribution via a calibration curve. However, only few calibration standards are commercially available and used to calibration of *SEC*. As the result the obtained molecular weights for polymers of different chemical composition then the one used to calibration of the equipment will be different then they really are. The highest differences are however observed for multibranched polymers where the molecular weights calculated according to calibration curves were considerably lower than the true values even if the analysed polymer and the calibration standard have the same chemical structure.

However, modern size exclusion chromatography can nowadays be equipped with a laser static light scattering detector. The scattering of the sample is measured as it passes through an appropriate sensor cell while illuminated by a high intensity beam of light. The high intensity light source is achieved by the use of a laser (light amplification by the stimulated emission of radiation) and also generates the light at the appropriate wavelength for measurements. The determination of molecular weight is then obtained without assumption or calibration curve so the absolute values for linear as well as branched polymers are obtained.

There are three forms of the detector: the low angle laser light scattering (*LALLS*) detector, right angle laser light scattering (*RALLS*) detector and the multiple angle laser light scattering

(*MALLS*) detector. All devices are commonly used but the multiple angle laser light scattering detector is more versatile. In addition to the molecular weight and its distribution *MALLS* detectors provide information about structure, radius of gyration, branching, aggregation, conformation or stability of the polymers.

4.2. Matrix-Assisted Laser Desorption Ionization Time Of Flight Mass Spectrometry (*MALDI-TOF-MS*)

MALDI-TOF-MS is now one of the most efficient analytical techniques for determining the absolute molecular weight of narrowly distributed macromolecules i.e. obtained by controlled polymerisation techniques. This method is ideally suited for analysis because of the simplicity of the mass spectra, which show mainly single-charged quasi molecular ions with hardly any fragmentation. Additionally, the time-of-flight analyser allows to analyse polymers with molecular weights beyond 1 MDa.

In traditional mass spectrometric analysis, analyte ions are normally produced by matrix-assisted laser desorption ionisation (*MALDI*) yielding very high selectivity results [233] . In the basic *TOF* instrument ions are formed in the ion source by a laser pulse, then rapidly accelerated to a high kinetic energy (20-30 keV). In a linear *TOF* instrument, once ions leave the short acceleration region, they travel down a 1-2 meter tube to the detector, where their arrival is timed. Mass-to-charge ratio *m/z* is determined from the time elapsed from ion formation (laser pulse) to ion arrival time at the detector. Ions typically enquire enough internal energy at the time of ionisation to undergo unimolecular decomposition as they travel along the flight tube; in a linear instrument, however, both intact ions and any fragment ions and neutrals arrive at the detector at virtually the same time. As the result only one peak is detected, at a time corresponding to the precursor ion mass.

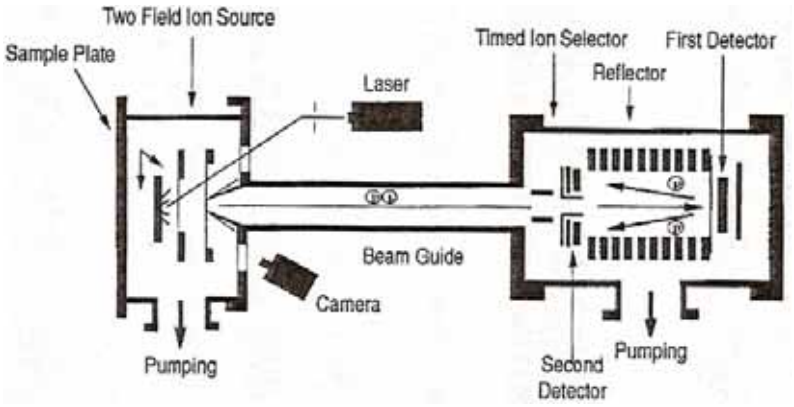


Figure 4.1. Schematic view on *MALDI-TOF-MS* set up.

Some *TOF* instruments are equipped with an electrostatic mirror (reflector) that reflects ions back toward a second detector, what is schematically presented in Figure 4.1. [234]. The original function of the reflector is to reduce the translational kinetic energy spread of the ions so as to improve the resolution. Faster ions penetrate further into the reflecting field and thus travel a longer distance than slower ions. As a result, if instrument parameters are set properly, all ions of the same *m/z* arrive at the detector at nearly the same time.

The selection of an appropriate *MALDI* matrix, cationization salt and sample preparation technique are critical factors to obtain a reliable mass spectrum and to infer structural information such as monomer masses and end groups. Generally, it is recommended to match the matrix polarity with the polymer under investigation. Nevertheless, matrix selection and optimisation for polymer analysis is still often a trial and error process, where some suggestions can be found in the literature [235]. Most of the synthetic polymers having heteroatoms will show cationization after addition of sodium or potassium salts, e.g. polyethers, polyesters [235]. Polymers without heteroatoms such as polystyrene can be successfully ionised after the addition of silver or copper salts, which interacts with the double bonds of these polymers [235]. It should be mentioned that for relatively polar polymers sodium and/or potassium adduct ions can be observed in the *MALDI* mass spectrum, even when they were not intentionally added. These cations are present as impurities in glassware, solvents, reagents, etc. And polymers having relatively high cation affinities do not necessarily require high cation concentration in the *MALDI* sample.

There are also many procedures used upon preparation of samples for *MALDI* analysis as dried-droplet method (air-drying of sample), fast crystallization method (vacuum removal of solvent), thin-layer method (application by spin-coating), electrospray deposition method etc. However, the microscopy analyses showed the best homogeneity of the samples prepared by fast crystallization methods.

4.3. Atomic Force Microscopy *(AFM)* [236]

Atomic force microscopy *(AFM)* is one of scanning probe microscopy techniques (*SPM*), which is a general term, used to describe a growing number of techniques that scan over a surface and measure its properties. Rather than using a beam of light or electrons, *SPM* uses a fine probe that scans over a surface, thus, there are no restrictions, concerning the wavelength of light or electrons. The resolution obtainable with this technique can resolve atoms, and true 3-D maps of surfaces, where the measurements can be carried out in air, vacuum or in liquid.

Additionally, it is also the foremost tool for the manipulation of matter at the nano-scale range.

The example set of *AFM* is presented in Figure 4.2. A common *AFM* device comprises a multisectional piezo element which allows the cantilever to move in x, y, and z direction, depending on bias applied to it. It determines motions of a cantilever (a plate-like spring) with a probing tip or (in some microscopes) the piezo moves the sample. The key part of *AFM* set up is the cantilever with attached tip used to scanning of the sample surface.

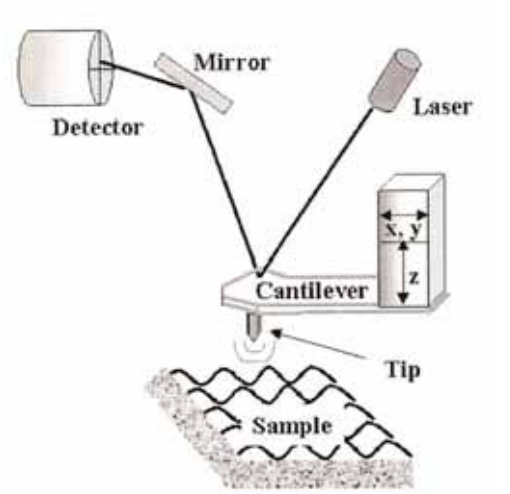


Figure 4.2. Schematic view on an *AFM* set up.

Generally, upon measurement the sharp tip is scanning the surface and forces between the samples and scanning probe are measured. Usually, the tip is brought close of the sample surface, while the force between the tip and the surface leads to the deflection of the cantilever according to Hooke's law. Depending on the type of the scanning process the tip and the sample remain in close contact during the scanning proceeds (*contact mode*) or the cantilever, equipped with the tip, is oscillated at the frequency near its resonance and touches the surface at the bottom of each oscillation for very small fraction of its oscillating period (*tapping mode*).

Recently, the *tapping mode* technique was developed and become more commonly used in *AFM* measurements. Unlike to *contact mode*, when the tip contacts the surface, which has to be quite smooth, it has sufficient oscillation to overcome the tip-sample adhesion forces. The surface material is not pulled sideways by the shear forces since the applied force is vertical. Although there is still contact with the sample, the reduction of contact time allow drastically reduce the undesired lateral forces and the good quality images are obtained. However, in that techniques slightly lower scan speed in comparison to *contact modes* can be applied.

4.4. Static Light Scattering (*SLS*) [237-238]

Light scattering is a convenient method which provides information about the weight-average molecular weight (M_w) of the macromolecule. However, the spatial expansion, i.e. radius of gyration (R_g) and/or distance of the dissolved macromolecules and their geometric shape can be also determined using this method.

In the static light scattering method, measurements are made of the scattered light intensities, i.e. Rayleigh scattering for small particles with dimension smaller than a twentieth of the wavelength ($d < \lambda/20$) and Debye scattering as a function of angle and concentration of polymers for larger particle ($d > \lambda/20$). Generally, when the monochromatic light beam passes through polymer solution it is weakened by absorption and scattering. It contacts with the molecules and induces a dipole moment (as a results of electron oscillation of outer shell), which becomes the source of the scatter intensity. In case of polymers which are big molecules with different chain geometry, many scattering centres may be distinguished in the molecule. As the result for the characteristic dimension of scattering macromolecules $d > \lambda/20$, the intensity of scattered light is dependent on the observation angles and usually scattering intensity decreases with increase of observation angle θ.

Taking into account polydispersity of the sample, the scattering intensity from the diluted polymer solution may be given by equation 4.1.

$$\frac{K \cdot c}{R_\theta} = \frac{1}{M_w}\left[1 + \frac{< R_g >_Z}{3} q^2\right] + 2A_2 c \qquad \textbf{(4.1.)}$$

$<R_g>_z$ - the *z*-average radius of gyration
K - optical constant
c - polymer concentration
A_2 - second virial coefficient
θ - scattering angle between incident and scattered light
M_w - weight molecular weight of polymer
$R_{(\theta)}$ - reduced intensity of scattered light

The most common method used for the evaluation of data obtained from light scattering measurements is the Zimm method [220-221], where the measurement of the scattering intensity as the function of angle and concentration lead to so-called Zimm plots. The second virial coefficient (A_2) and radius of gyration $<R_g>_z$ can be obtained when the polymer concentration

and the scattering angle approach zero, respectively. Additionally, M_w can be calculated from Kc/R_θ for c = 0 and q = 0. Since samples are usually not monodisperse systems, the values of M_w, R_g or A_2 are the averaged values.

4.5. Dynamic Light Scattering *(DLS)* [237-238]

Dynamic light scattering (*DLS*) uses the time dependence of the intensity of the scattered light to observe the dynamic behaviour of the chain molecules and to determine the translational diffusion coefficient of small particles. This method works well for sub-micron particle dimensions, sometimes with particles up to a few microns in diameter. The smallest particle size, able to be determined using dynamic light scattering, depends on the scattering properties of the particles (relative refractive index of particle and medium), the incident light intensity (laser power and wavelength) and the detector/optics configuration.

Although the principles of *DLS* are similar to *SLS*, in case of *DLS*, detected fluctuations are measured within time intervals as short as 100 ns, which exactly corresponds to the Browian motions of the particles. When a colloidal dispersion is lasered, the wavelength of light is changed thus, it is possible to observe time-dependent fluctuations in the scattered intensity.

The fluctuations in the scattered intensity arise from the constantly varying distances between particles due to thermal (Brownian) motion. Constructive and destructive interference of light scattered by neighbouring particles within the illuminated zone gives rise to the intensity fluctuations at the detector plane which, as it arises from particle motion, contains information about this motion. Since fluctuation correlates with each other, the dynamics of the polymer solution (the diffusion coefficient) can be investigated by the autocorrelation function *C(t)*.

$$C(t) = \exp(-D_T q^2 t) \qquad \textbf{(4.2.)}$$

C(t) - autocorrelation function
D_T - translation diffusion coefficient
q^2 - magnitude of scattering vector
t - time

In the simplest case, for small monodispersed particles, autocorrelation function can be presented as an exponential function of decay time (equation 4.3.).

$$C(t) = \exp^{-\Gamma t} \qquad \textbf{(4.3.)}$$

Γ - the first decay time

Analysis of the time dependence of the intensity fluctuations yield the diffusion coefficient of the particles, from which the hydrodynamic radius or diameter of the particles can be calculated according to the Stokes-Einstein equation 4.4.

$$R_h = \frac{k_b T}{6\pi\eta_A D_T} \qquad \textbf{(4.4.)}$$

R_h - hydrodynamic radius
k_b - Boltzman's constant
T - absolute temperature in Kelvin
η_A - solvent viscosity
D_T - translation diffusion coefficient

Also particle size distribution is determined from the analysis of the autocorrelation function, by numerical fitting of the data using calculations based on assumed distributions. A monodisperse sample shows a single exponential decay and fitting of a calculated particle size distribution to this curve is relatively easy. However in practice, polydispersed samples give a series of exponentials. As the result several complex schemes have been used to fit the calculated data to the suitable curves, while in this work the CONTIN method was used.

The very useful tool for estimation of the particle architecture in solution is the so-called ρ-*parameter*. It can be calculated based on *DLS* and *SLS* measurements, as the ration of R_g and R_h (equation 4.5.).

$$\rho = \frac{R_g}{R_h} \qquad \textbf{(4.5.)}$$

As ρ parameters for polymers of different structures were already presented in the literature, the simple comparison of experimental data with available values gives the polymer shape in the solution.

5. Experimental procedures

5.1. List of materials

Acetic anhydride, 98 %	(POCh)
4,4'-Azobis(*4*-cyanovaleric acid) (*AVA*), 98 %	(Aldrich)
α,α'-Azo-bis-isobutyronitrile (*AIBN*), 97 %	(Aldrich)
Benzene (C_6H_6), p. a.	(POCh)
2-Bromopropionyl bromide, 97 %	(Aldrich)
Calcium hydride (CaH_2), p. s.	(Aldrich)
Calcium oxide (CaO), 96 %	(J. T. Backer)
Chloroform, p.a.	(Aldrich)
Chloroform-d_6 ($CDCl_3$), 99,8 %	(Deutero)
p-(Chloromethyl) styrene, 96 %	(Aldrich)
Copper bromide (CuBr), 99,995%	(Aldrich)
Charcoal	(Aldrich)
2,5-Dihydroxybenzoic acid (*DHB*)	(Bruker Daltonics)
1,6-Diphenyl-*1,3,5*-hexatriene (*DPH*), 98 %	(Aldrich)
Dichloromethane	(Aldrich)
Dimethyl formamid (DMF), p. s.	(Merck)
Dimethy sulfoxid (DMSO), p. s.	(Merck)
Deuterated dimethyl sulfoxid (DMSO-d_6), 99,8%	(Deutero)
Dowex monosphere 650 (H) cation exchange rein	(Aldrich)
Dowex monosphere 550 (OH) anion exchange rein	(Aldrich)
Dowex MSC-1 cation exchange rein	(Aldrich)
Formic acid, 85%	(Roth GmbH)

Formaldehyde, 37%	(Roth GmbH)
Ethyl vinyl ether, 99%	(Fluka)
Ethyl acetate	(Aldrich)
Glycidol (*2,3*-epoxypropanol-*1*), 96%	(Aldrich)
Hexane	(Aldrich)
Hydrochloric acid (HCl), 37 %	(Merck)
Nitric acid (HNO_3), p.a.	(Acros)
Lithium bromide (LiBr) p.a.	(Aldrich)
Methanol, p.a.	(Aldrich)
Methanol-d_6 (CD_3OD), 99,8 %	(Deutero)
Magnesium sulphate ($MgSO_4$), p.a.	(Merck)
Sodium hydride (NaH), pure	(Fluka)
Sodium hydroxide (NaOH), p.a.	(J. T. Baker)
Oxalic acid ($(C_2H_2O_4)_2$), pure	(Fluka)
Polyethylene oxide (PEG M_n=2000 g/mol)	(Aldrich)
Phenyl glycidyl ether, 98 %	(Fluka)
Potassium *tert*-butoxide (*t*BuOK), 99%	(Fluka)
Pyridine, pure	(Aldrich)
Silica gel 60 (0,04 – 0,63 mm)	(Merck)
p-Toluene sulphuric acid, 98%	(Acros)
Tertahydrofuran (THF), p.a.	(POCh)
Triethylamine, 98%	(Fluka)
Tris-(*2*-aminoethyl-amine) (*TREN*), 96%	(Aldrich)
Deuterated water (H_2O-d_6), 99,9 %	(Deutero)

5.2. Purification procedures

5.2.1. Solvents

Tertahydrofuran (THF) for anionic polymerisation was dried over CaH_2 and refluxed over Na/K alloy in nitrogen atmosphere.

Methanol, hexane, ethyl acetate, benzene were purified by distillation.

DMF and DMSO were purified by distillation under reduced pressure (p = 40 mbar).

All deuterated solvents were used as received.

5.2.2. Reagents

1-Ethoxyethyl glycidyl ether (glycidol acetal) was synthesized as described by Fitton *et al.* [216]. The obtained monomer was dried over CaH_2, stored under reduced pressure in the ampule over CaH_2 and before each polymerisation freshly distilled.

Phenyl glycidyl ether was dried over CaH_2 and distilled three times to give fraction of the purity 99,7 %. It was stored over CaH_2 and freshly distilled before each polymerisation.

Initiators of conventional radical polymerisation *α,α'*-azo-bis-isobutyronitrile (*AIBN*) and *4,4'*-azobis(*4*-cyanovaleric acid) (*AVA*) were crystallized from methanol.

Glycidol (*2,3*-epoxypropanol-1) was dried over molecular sieves (4Å) for few days and distilled over CaH_2 under reduced pressure.

Ethyl vinyl ether was purified by distillation under dry nitrogen.

2-Bromopropionyl bromide and *p*-(chloromethyl)styrene were distilled under reduced pressure prior to use.

p-Toluene sulphuric acid was dried overnight under reduced pressure at 40ºC.

Triethylamine was dried over CaH_2 and distilled over it at atmospheric pressure, prior to use.

Tris-(*2*-aminoethyl-amine) (*TREN*), formic acid, formaldehyde and acetic anhydride were used as received.

Sodium chloride (NaCl), sodium hydroxide (NaOH), magnesium sulphate ($MgSO_4$), sodium hydrate (NaH), calcium oxide (CaO), oxalic acid ($(C_2H_2O_4)_2$), copper bromide (CuBr), potassium *tert*-butoxide (*t*-BuOK), calcium hydride (CaH_2), lithium bromide (LiBr), polyethylene oxide (PEG 2000), *1,6*-diphenyl-*1,3,5*-hexatriene (*DPH*), *2,5*-dihydroxybenzoic acid (*DHB*) were used as received.

Ion exchangers were regenerated with 5 wt-% solution of HCl or NaOH in case of cation and anion exchanger, respectively.

Concentrated hydrochloric acid (HCl) was diluted with water to give 5 wt-% solution.

Dowex MSC-1 resin was regenerated using 1,6 M HNO_3 and dried at 50ºC.

Silica gel 60 (0,040-0,063 mm) and charcoal were used as received.

5.2.3. Fractionation of the polymacromonomers

Two different methods were used to separate unreacted oligomer from obtained polymacromonomer: selective precipitation and dialysis in methanol.

In the first separation method 1 g of the polymerisation product was dissolved in 5 mL of methanol and precipitant - acetone - was added until the solution turned distinctly cloudy. The precipitated fraction was separated by decantation of the liquid and dried to give 0,5 g of pure polymacromonomer. Liquid was evaporated to give 0,45 g of low molecular weight oligomer.

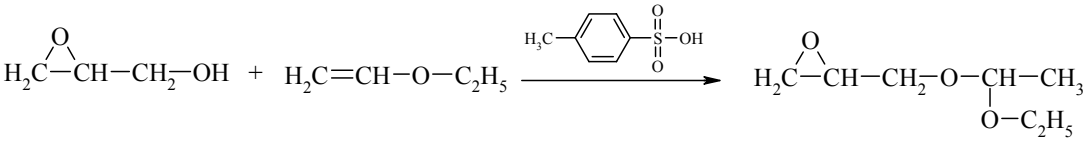
In the second method a methanol solution of the polymerisation product was dialyzed in methanol through a SpectraPor membrane with an exclusion limit of 50 000 g/mol. The dialysis was carried out for 5 days. After the removal of solvents 0,55 g of polymacromonomer and 0,4 g of low molecular weight fraction was obtained.

In case of polymacromonomer obtained by polymerisation of PGlPhE-*b*-PGl-St the product of reaction was insoluble in methanol (as well as in water) so purification by described methods was not possible. However, it could be fractionated by precipitation from DMF to water. For this purpose 1 g of the polymerisation product was dissolved in 10 mL of DMF and added drop wise to 100 mL of water. The precipitated polymacromonomer was filtrated under reduced pressure. That procedure was repeated three times to give 0,45 g of polymacromonomer and 0,4 g of low molecular weight fraction.

5.3. Syntheses

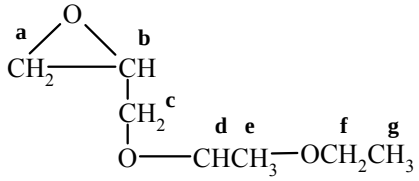
5.3.1. 1-Ethoxyethyl glycidyl ether (glycidol acetal)

Glycidol and ethyl vinyl ether were reacted to glycidol acetal using *p*-toluenesulfonic acid as catalyst as presented in Scheme 5.1.



Scheme 5.1. Synthesis of glycidol acetal according to Fitton *et al*. [216]

In an example preparation, 350 mL (5,23 mol) of freshly distilled glycidol and 1700 mL (17,8 mol) of ethylvinyl ether were added to 3000 mL three-neck flask equipped with thermometer, N_2 gas inlet/outlet and magnetic stirrer. The reaction mixture was cooled down in an ice bath to ~ 0 °C. As next 8 g (0,046 mol) of *p*-toluene sulphuric acid was introduced into the flask within about two hours, to prevent overheating of the reaction mixture. The reaction was continued under stirring at room temperature for approximately 3h to reach high conversion of glycidol (indicated by gas chromatography). As next, the reaction mixture was alkalised by extraction with an excess of saturated $NaHCO_3$ (glycidol acetal in unstable in acidic conditions) and the organic phase was collected and dried over magnesium sulphate. The solid was filtrated off and excess of ethyl vinyl ether was removed under reduced pressure. The obtained crude product was fractionated under reduced pressure to obtain the monomer with 99,8 % purity (indicated by gas chromatography). Yield: 96% of crude product, 70% after fractionation (purity 99,8%).



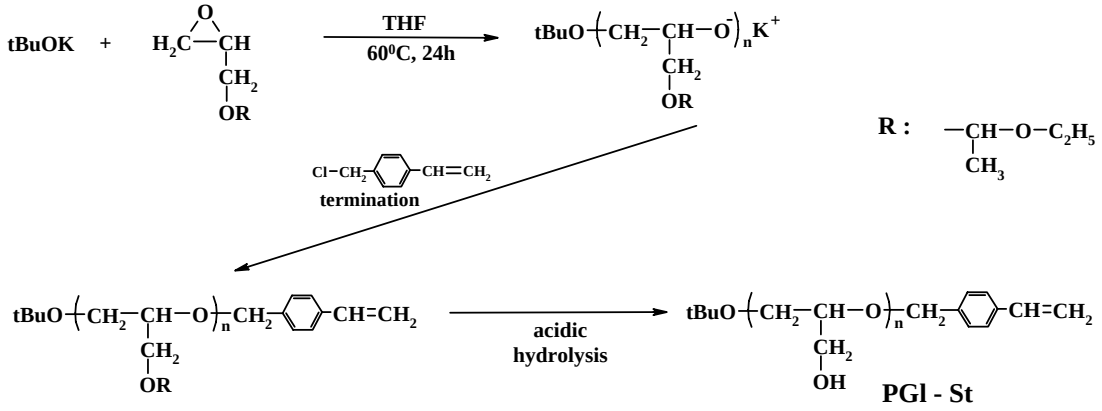
^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) (**g**) 1,1-1,5 (t, CH_3); (**e**) 1,2-1,25 (q, CH_3); (**f**) 2,5-2,8 (m, CH_2); (**a, b, c**) 3,1-3,8 (m; CH, CH_2); (**d**) 4,7-4,75 (m, CH).

5.3.2. Poly(glycidol)-based macromonomers

5.3.2.1. *α-t*–butoxy-ω-vinylbenzyl-poly(glycidol)

Poly(glycidol) macromonomers were obtained in two different synthesis routes: by direct termination of living macroanion with termination agent according to literature [239] and by modification of *ω*-hydroxyl group of anionically obtained poly(glycidol acetal).

- ***Direct termination of living macroanion***



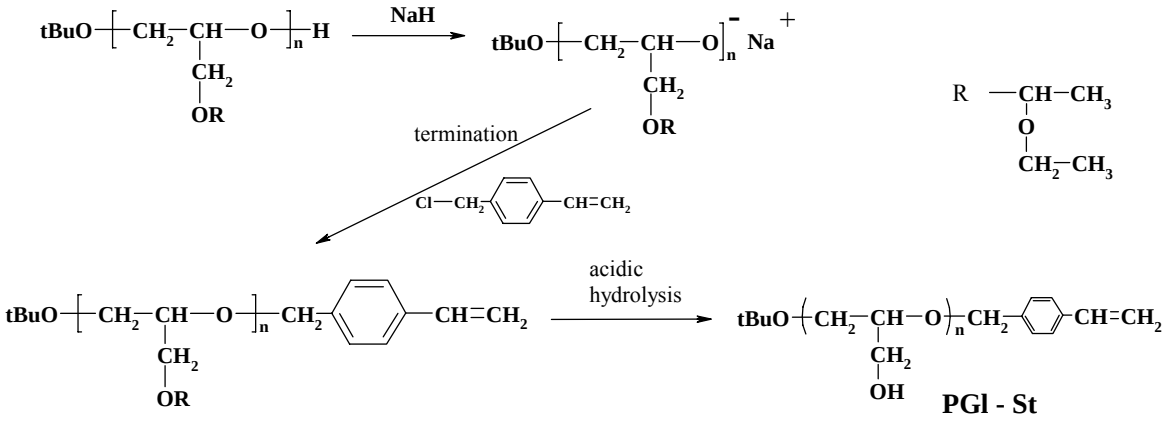
Scheme 5.2. Synthesis of PGl-St by termination method.

For a typical example: 0,8 g (7,2 mmol) of initiator potassium *t*-butoxide was placed under dry nitrogen in a dry reactor and 15 mL of dry THF was added to dissolve the initiator. As next, 54 g (0,37 mol) of glycidol acetal was distilled into the ampule under reduced pressure, diluted with 20 mL of dry THF and slowly added to the cooled reactor with initiator solution. The polymerisation was carried out for 24 h at 60 ºC. Its progress was checked by gas chromatography. To introduce the polymerizable group the living polymer chains were terminated with excess of *p*-(chloromethyl)styrene. After removal of THF the product containing *α-t*-butoxy-*ω*-vinyl benzyl-poly(glycidol acetal), further referred to as PGlAc-St, was obtained with 99 % yield.

In order to remove excess of terminating agent the resultant PGlAc-St was purified by chromatography. Macromonomer was dissolved in hexane and passed through the column with silica gel 60. It was observed that PGlAc-St absorbs on the silica gel, while *p*-(chloromethyl)styrene migrates with hexane. When the whole unreacted terminating agent was removed from the column solvent was changed to polar ethyl acetate to elute the macromonomer. After removal of solvents pure PGlAc-St was obtained with 85 % yield.

- ***Modification of ω-hydroxyl group***

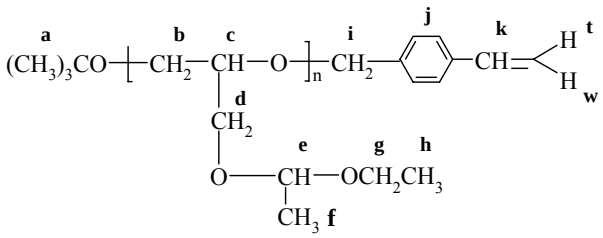
Anionic polymerisation of glycidol acetal was carried out as described above in THF for 24 h. After that time the living polymer was terminated by addition of several drops of distilled water (0,5 molar excess in respect to active centres) in order to obtain hydroxyl-terminated poly(glycidol acetal). Formed KOH was removed by ion exchanger Dowex and resulted polymer was dried to the equal mass and used to modification as presented in Scheme 5.3.



Scheme 5.3. Synthesis of PGl-St by modification of hydroxyl group.

For a typical example: 5 g (0,034 mol, 68 mmol hydroxyl groups) of ω-hydroxyl poly(glycidol acetal) was dissolved in 20 mL of dry THF in nitrogen atmosphere. In dry reactor 0,08 g NaH (3,55 mmol, 5 times the molar amount in respect to ω-hydroxyl group from poly(glycidol acetal)) was suspended in 20 mL of dry THF and the solution of *ω*-hydroxyl poly(glycidol acetal) was added. The resulted suspension was stirred for 24 h at room temperature. As next temperature was raised to 50 °C and a solution of *p*-(chloromethyl)styrene in 10 mL of dry THF was added. The reaction mixture was stirred for additional three hours. The solids were filtered off and the resulted macromonomer was purified by chromatography as described above.

The structure of obtained macromonomers was confirmed by ^{1}H NMR spectroscopy.

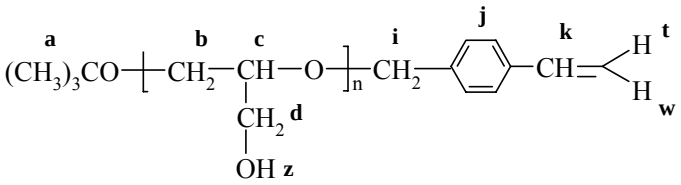


^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) (**a, f, h,**) 1,12 – 1,25 (CH_3, m); **(b, c, d, g)** 3,45-3,65 ($3CH_2$, CH, m); **(e, i)** 4,63-4,72 (CH, m); **(j)** 7,25-7,4 ($4CH_2$ ar., dd); (**k**) 6,6-6,7 (CH_2, q); **(t)** 5,25-5,3 (CH, d); **(w)** 5,65-5,7 (CH, d)

- ***Hydrolysis of acetal groups***

The protecting acetal groups of poly(glycidol) macromonomers were removed under acidic conditions. 20 g of the polymer was dissolved in 200 mL of methanol. To the reaction mixture 12,3 g of oxalic acid dissolved in 50 mL of methanol was added. After 1 h solid CaO was incorporated to the reaction mixture to give pH = 11. Insoluble salts and the access of CaO were filtrated and the filtrate was neutralized with 5 % HCl to give pH = 7. Solvents were evaporated. Afterwards the hydrolysed oligomer was dissolved in water and desalinated using ion exchangers. *α-t*–butoxy-*ω*-vinylbenzyl–poly(glycidol), further referred to as PGl-St, was obtained with 90 % yield.

The structure of obtained macromonomers was confirmed by ^{1}H NMR spectroscopy.



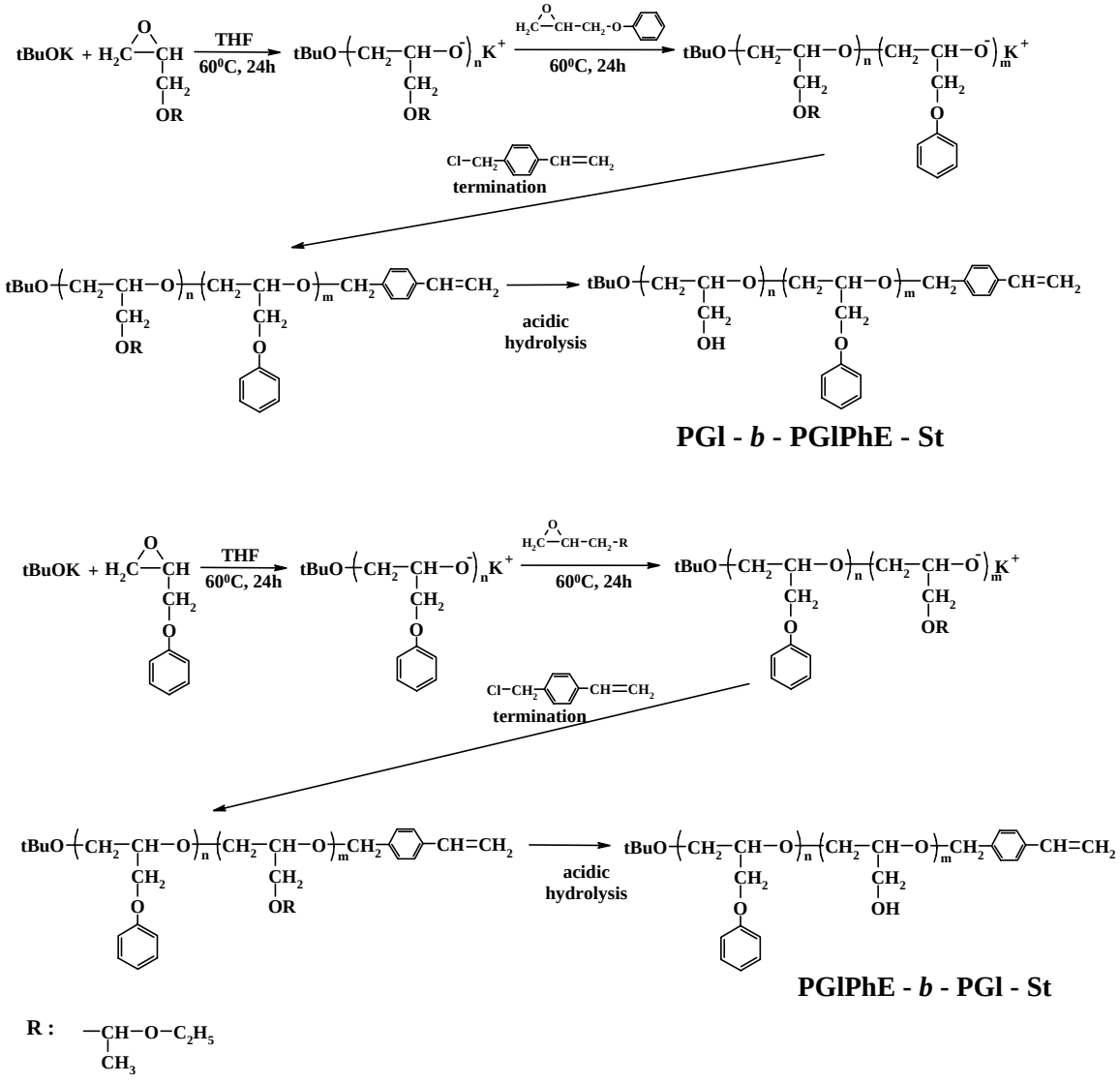
^{1}H NMR (DMSO, 500 MHz): δ (ppm) (a) 1,12 – 1,25 (CH_3, m); (b, c, d) 3,45-3,65 ($3CH_2$, CH, m); (z, i) 4,63-4,72 (CH, m); (j) 7,25-7,4 ($4CH_2$ ar., dd); (k) 6,6-6,7 (CH_2, q); (t) 5,25-5,3 (CH, d); (w) 5,65-5,7 (CH, d)

5.3.2.2. Block macromonomers of glycidol and phenyl glycidyl ether

Block macromonomers of glycidol acetal and phenyl glycidyl ether were obtained using living anionic copolymerisation. To synthesize the polymer chain sequential monomer addition was applied as presented in the Scheme 5.4.

For a typical example: 25 g (170 mmol) of glycidol acetal was freshly distilled under reduced pressure into a dry ampule and dissolved in 25 mL of dry, freshly distilled THF. 0,32 g (2,8 mmol) of potassium *t*-butoxide was added to the reactor under dry nitrogen atmosphere, degassed in high vacuum and dissolved in 25 mL of dry THF. To the solution of the initiator the monomer was added and the reactor was placed in a thermostated bath at 60 °C for 20 hours. Full conversion of the first monomer (after 20 h) was confirmed by gas chromatography and the second monomer (phenyl glycidyl ether) was added. 4,3 g (30 mmol) of dry phenyl glycidyl ether was distilled under reduced pressure to a dry ampule and dissolved in 5 mL of dry THF. The solution of second monomer was added to the solution of

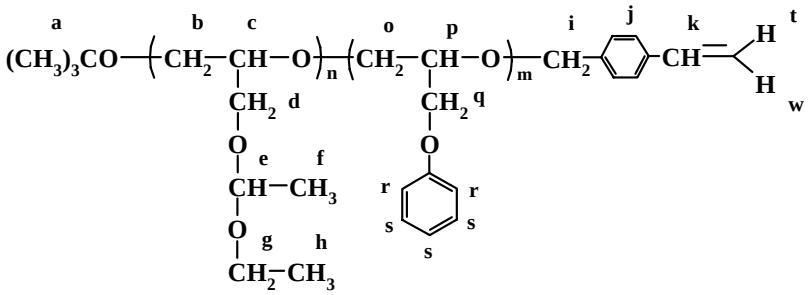
the living chains of poly(glycidol acetal) under reduced pressure and placed in a thermostated bath at 60 °C for 15 hours. During this time, full conversion of the monomer was obtained (confirmed by gas chromatography). The living block macroanions were terminated with 0,38 mL (3 mmol) of *p*-(chloromethyl)styrene. THF was evaporated to give 29 g of a bright yellow sticky oil. The block macromonomer *α-t*-butoxy-*ω*-vinylbenzyl-poly(glycidol acetal)-*block*-poly(phenyl glycidyl ether) (PGlAc-*b*-PGlPhE-St) was obtained with 99 % yield. The resultant macromonomer was purified from unreacted *p*-(chloromethyl)styrene by chromatography in the way described for PGlAc-St.



Scheme 5.4. Synthesis of block macromonomers of glycidol and glycidyl phenyl ether.

Macromonomer *α-t*-butoxy-*ω*-vinylbenzyl-poly(phenyl glycidyl ether)-*block*-poly(glycidol acetal) (PGlPhE-*b*-PGlAc-St) was obtained in an analogous way using the opposite sequence of monomer addition.

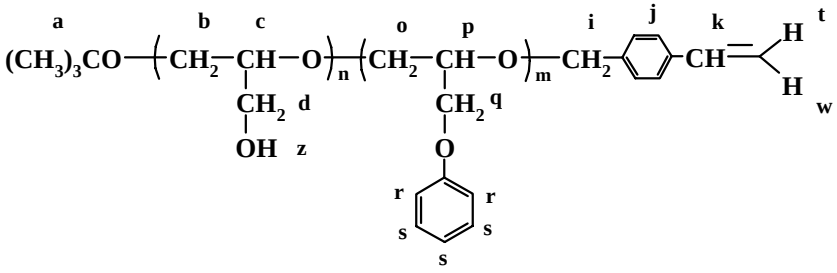
The structure of obtained macromonomers was confirmed by ^{1}H NMR spectroscopy.



^{1}H NMR (DMSO, 500 MHz): δ (ppm) (**a, f, h,**) 1,12 – 1,25 (CH_3, m); **(b, c, d, g, o, p, q)** 3,45-3,65 ($3CH_2$, CH, m); **(e, i)** 4,63-4,72 (CH, m); **(j)** 7,25-7,4 ($4CH_2$ ar., dd); (**k**) 6,6-6,7 (CH_2, q); **(t)** 5,25-5,3 (CH, d); **(w)** 5,65-5,7 (CH, d); **(r)** 7,2-7,3 (CH_2 ar., m); **(s)** 6,8-6,95 (CH_2 ar., m).

- ***Hydrolysis of acetal groups***

Hydrolysis of protecting acetal groups from glycidol acetal was carried out as described before to give 14,5 g of a bright yellow sticky polymer (yield 85 %) with the exception that products were desalinated by dialysis through a SpectraPor membrane with an exclusion limit of 3500 g/mol. The deprotected polymers are denoted as PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St, respectively.



^{1}H NMR (DMSO, 500 MHz): δ (ppm) (**a**) 1,12-1,25 (CH_3, m); **(b, c, d, o, p, q)** 3,45-4,1 (CH_2, CH, m); **(z, i)** 4,63-4,72 (CH, m); **(j)** 7,25-7,4 ($4CH_2$ ar., dd); (**k**) 6,6-6,7 (CH_2, q); **(t)** 5,15-5,25 (CH, d); **(w)** 5,65-5,7 (CH, d); **(r)** 7,2-7,3 (CH_2 ar., m); **(s)** 6,8-6,95 (CH_2 ar., m).

5.3.3. Polymacromonomers

5.3.3.1. Conventional radical polymerisation

Conventional radical homopolymerisation of all obtained macromonomers was carried out in two different systems: (1) in water with *4,4'*-azobis(*4*-cyanovaleric acid) (*AVA*) as initiator; (2) in water-benzene mixture using *2,2'*-azo-bis-isobutyronitrile (*AIBN*) as initiator.

Additionally in case of block macromonomers PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St polymerisation was carried out in THF with *2,2'*-azo-bis-isobutyronitrile (*AIBN*) as initiator.

- ***Polymerisation in water***

The macromonomer (the amount varied from 0,25 g to 2 g) and 1,4 mg (0,005 mmol) of *AVA* were placed in a 10 mL glass reactor, dissolved in 2 mL of bidistilled water and stirred overnight. Air was removed from the reaction mixture by three freeze-thaw cycles and the reactor was purged with nitrogen. The polymerisation was carried out in an oil bath at 60 °C for 24 h. After reaction the solvents were evaporated and the samples analysed.

- ***Polymerisation in water-benzene mixture***

1 mg (0,005 mmol) of *AIBN* was placed in a 10 mL glass reactor and dissolved in 0,2 mL of benzene. A proper amount of macromonomer (varied from 0,25 g to 2 g) was dissolved in 2 mL of bidistilled water and added to the initiator solution. The mixture was intensively stirred overnight. After air was removed by three freeze-thaw cycles the reaction mixture was purged with nitrogen and placed in an oil bath at 67 °C for 24 h. After polymerisations the solvents were evaporated and the samples analysed.

- ***Polymerisation in THF***

The block macromonomer (amount varied from 0,25 g to 2 g) and 1,4 mg (0,005 mmol) of *AIBN* were placed in a 10 mL glass reactor, dissolved in 2 mL of THF and stirred overnight. After removal of air by three freeze-thaw cycles the reactor was purged with nitrogen and placed in an oil bath of 67 °C for 24 h. After polymerisation the solvents were evaporated and the samples analysed.

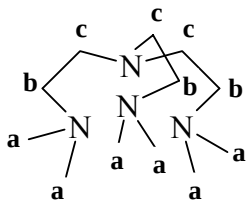
5.3.3.2. Controlled radical polymerisation

ATRP polymerisation of macromonomers was carried out in water with α-methyl-ω-*2*-bromopropionate polyethylene oxide macroinitiator and *Me_6TREN* (*tris*-(*2*-dimethylaminoethyl)) as ligand. Both macroinitiator [240] and ligand [192] were synthesised according to literature as described below.

- ***Synthesis of ligand Me_6TREN***

In an example preparation: the mixture of 3 mL (2,2 mmol) *tris*-(*2*-aminoethyl) amine and 2,3 mL (130 mmol) of water was added drop-wise to a solution of 16 mL (266 mmol) of formic acid (85%) and 13 mL (144 mmol) of formaldehyde (37%). Initially the reaction mixture was kept in an ice bath (strong exothermic effect) and additionally left stirred for 1 h at room temperature. Next, it was immersed in oil bath and heated for 6 h at 120 °C. The unreacted formic acid and formaldehyde were removed under reduced pressure and the residual liquid phase was adjusted to pH = 10 with 10% NaOH solution. Afterwards the water solution of *Me_6TREN* was extracted five times with CH_2Cl_2 and organic layer was collected and dried over $MgSO_4$. After removal of dichloromethane the residue was distilled under vacuum to give 3,1 g of colourless liquid (75% yield).

The structure of obtained ligand was confirmed by ^{1}HNMR.



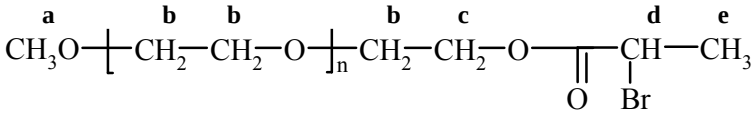
^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): (**a**) 2,2 (m, CH_3); (**b**) 2,39 (m, CH_2); (**c**) 2,6 (m, CH_2).

- ***Synthesis of macroinitiator***

For a typical example, in 250 mL three-neck flask, PEO_{47}-OH (10 g, 4,8 mmol) was dissolved in 100 mL of toluene. After azeotropic distillation of 50 mL of toluene in inert atmosphere (to reduce traces of water), 1,3 mL (9,6 mmol) of triethyl amine was added. The solution was cooled to 0 °C and 1,2 mL (10 mmol) of *2*-bromoisobutyryl bromide was added drop wise over 1 h, and the reaction mixture was left stirring at room temperature for 24 h. The obtained solution was treated with charcoal, which was subsequently removed by filtration. After removal of most of the

toluene solution of macroinitiator was precipitated into 10-fold excess of ether. The crude product was dried under vacuum, dissolved in water at pH = 8-9, and then extracted three times with dichloromethane. The organic layers were collected and dried over $MgSO_4$, and removal of the solvent under vacuum afforded 8 g of the purified macroinitiator with 80 % yield.

The structure of the obtained macroinitiator was confirmed by ^{1}H NMR spectroscopy.



^{1}H NMR ($CDCl_3$, 500 MHz), δ (ppm): (**e**) 1,83-1,86 (CH_3, d) (**a**) 3,4 (CH_3, s); (**b)** 3,55-3,85 (CH_2, m); (**c**) 4,35-4,4 (CH_2, m); (**d**) 4,6-4,65 (CH, q)

- ***Preparation of complex Cu^I-Me_6TREN***

0,11g (0,48 mmol) of *Me_6TREN* and 0,047g (0,48 mmol) of CuBr was introduced to the 10 mL glass reactor under nitrogen atmosphere. Traces of oxygen were removed by threefold filling and evacuation of dry argon from the reactor. Next 1 mL of water degassed via three freeze-pump-thaw cycles was added and stirred for few minutes. The dark blue, heterogeneous solution of complex *Cu^I-Me_6TREN* was obtained and used to polymerisation.

- ***Polymerisation procedures***

A typical example: 1,5 g (0,3 mmol) macromonomer (PGl-St) and 0,055 g (0,027 mmol) macroinitiator was placed in 25 mL glass reactor and dissolved in 8 mL of bidistilled water. The solution was degassed by freeze-thaw cycles and left stirring overnight. Then 0,05 mL of freshly prepared *Cu^I-Me_6TREN* complex solution [8mg (0,054 mmol) of CuBr, 12,4 mg (0,054 mmol) of *Me_6TREN*] was added and colour turned to light blue. The reaction was carried out for 24 h at room temperature. After polymerisation copper was removed on cation exchanger, the solvents were evaporated and samples analysed.

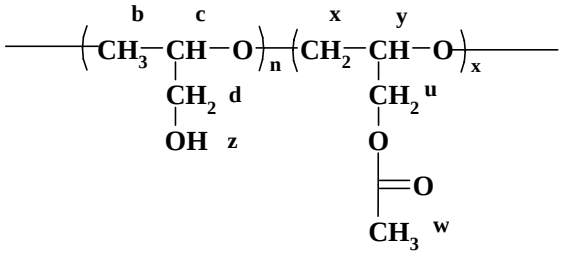
5.3.4. Temperature sensitive polymers

In order to obtain temperature sensitive compounds hydroxyl group of poly(glycidol) was esterified with acetic anhydride in DMF using pyridine as proton acceptor as described by Dworak *et al.* [241]. Both macromonomers and polymacromonomers were used to

esterification, where the degree of esterification was controlled varying the ratio of the acetic anhydride to the hydroxyl groups in the polymer.

For a typical example: 1g of macromonomer or polymacromonomer was placed in 25 mL round flask equipped with septum and dissolved in 10 mL of DMF. Next depending from the desired degree of esterification the proper amounts of pyridine and acetic anhydride were introduced. For instance when the theoretical degree of esterification was 75 % in respect to hydroxyl groups of polymacromonomers 0,76 mL (0,83 g) of acetic anhydride and 1,8 mL (0,173 g) of pyridine was added. The reaction was carried out for 24 h at 60 °C. After cooling solvents and unreacted compounds were evaporated. In case of polymacromonomers residue was additionally dissolved in water and dialysed from SpectaPor membrane of exclusion limit 3500 g/mol.

The introduction of acetic group to the polymer structure was confirmed by ^{1}H NMR.



^{1}H NMR (DMSO, 500 MHz): δ (ppm) **(b, c, d)** 3,45-3,65 (3CH_2, CH, m); **(z)** 4,63-4,72 (OH, m); **(x, y ,z)** 3,8-4,2 (3CH_2, m); (**w**) 1,9-2,0 (CH_3, s).

5.4. Measurements

- ***Atomic Force Microscopy (AFM)***

The surface topology of polymacromonomers as well as micelles on mica was observed using multimode AFM instrument (Digital Instruments, Santa Barbara) operating in the tapping mode. Silicon tips with radius of 10-20 nm, spring constant of 30 N/m, and resonance frequency of 250-300 kHz were used, correctly calibrated with gold nanoparticles (diameter 5 nm), in order to evaluate the tip radius. Samples were prepared by spin coating of the polymer solutions with concentration 0,001 g/L.

Adsorption of polymacromonomers from on silica wafers was also studied by AFM. As solvents water and DMSO were used, while the polymer concentration was 1 g/L.

- ***Differential Scanning Calorimetery (DSC)***

Calorimetric measurements of glass transition temperatures and phase transition temperatures of polymers were determined using 2920 Modulated Differential Scanning Calorimeter (TA Instruments). Upon transition temperature measurements scans were performed at heating rate of 30 °C/h in the range of temperatures –70 °C to 100 °C. Upon phase separation temperature measurements polymer solutions of concentration 5 g/L and 10 g/L were placed in DSC cells, sealed and scanned in a N_2 gas flow against an empty reference cell from 0 °C to 80 °C with heating rates 5 °C min^{-1}.

- ***Dynamic Light Scattering (DLS)***

DLS measurements were performed on a commercial laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000EP multiple digital correlator. Laser goniometer system ALV/CGS-8F S/N 025 with a helium-neon laser (Uniphase 1145P, output power of 22 mW, with λ = 632,8 nm) was used. Sample were passed through a 0,2 μm nylon membrane filter, transferred to 10 mm diameter test tube, immersed in thermostated toluene bath and measured, where angles of observation θ was varied from 30 to 110°.

- ***Gas Chromatography (GC)***

Conversion of glycidol upon synthesis of glycidol acetal was measured using VARIAN 3400 gas chromatograph with a J&W Scientific DB-5 (30 m x 0,32 mm) column.

- ***Matrix-Assisted Laser Desorption Ionisation Time Of Flight Mass Spectroscopy (MALDI-TOF-MS)***

MALDI-TOF-MS measurements were performed on BRUKER DALTONICS biflex IV equipment. Experiments were done on accelerating potential of 20 kV in the positive mode. Samples for measurements were prepared in methanol or in THF by mixing of 1 μL of macromonomer solution (C=10 g/L) with 9 μL of matrix solution containing potassium triflate (ratio K^+ : matrix = 1 : 9). As matrix 2,5-dihydroxybenzoic acid was used. A total of 1 μL of this mixture was deposited on the plate and, after evaporation of the solvent, measurements were performed under high vacuum. To produce the final spectrum, mass spectra from 150 shots were accumulated. Peptide calibration standard, received from Bruker Daltonics, was used as external standard.

- ***Nuclear Magnetic Resonance Spectroscopy (NMR)***

^{1}H NMR spectra were recorded using Brucker DRX 500 (500 MHz). DMSO-d_6, D_2O, CD_3OD, $CDCl_3$ were used as the solvents. The resonance are given in ppm referenced to the solvent peaks for DMSO-d_6 (δ (^{1}H) = 2,5 ppm), D_2O (δ (^{1}H) = 4,75 ppm), $CDCl_3$ (δ (^{1}H) = 7,25 ppm), CD_3OD (δ (^{1}H) = 4,85 ppm).

- ***Size Exclusion Chromatography with Multiangle Light Scattering Detection (SEC-MALLS)***

Size exclusion chromatography measurements were performed in THF at 30 °C using PSS-SDV 5μ columns: 10^5 Å, 10^3 Å, 2x100 Å or in N,N-dimethylformamide (DMF) with 5 mmol/L LiBr at 45 °C using a set of PSS GRAM 10μ columns: 10^3, 10^2 and 30 Å. All chromatograms were obtained at 1 mL/min flow. Differential refractometer Δn 1000 from WGE Dr. Bures was used as the concentration detector and the molecular weights were determined using the DAWN multi angle laser light scattering detector (MALLS) from Wyatt Technology Corporation and their Astra software.

- ***Static Light Scattering (SLS)***

The aqueous solution of macromonomers in the range 0,0044 g/L to 10 g/L were filtered using 0,1 μm nylon filters right to the 20 mm test tube, immersed in thermostated bath at 25 °C and measured with FICA 50 SLS apparatus equipped with a He-Ne laser (wavelength of

632 nm). The measurements were taken at observation angles θ = 90 ° (estimation of *CMC*) and at θ varying from 15 ° to 120 ° (molecular weights of micelles).

The refractive index increments (*dn/dc*) of macromonomers in water were measured at 25 °C with a refractometer FICA 50.

- ***Surface tension***

Surface tension measurements of the series of aqueous solutions of macromonomers in the concentration range of 0,0044 to 10 g/L were taken at 25 °C on the DSA KRUSS INSTRUMENT tensiometer.

- ***UV-VIS Spectroscopy***

UV-VIS Lambda 19 (Perkin-Elmer) spectrometer coupled to a temperature controller was used to investigate the phase transition behaviour of temperature sensitive polymers. The 0,5 cm long sample cell, containing approximately 2 mL of polymer solution was used, against distilled water as a reference. Polymer concentration was constant, and kept on the level 5 g/L for macromonomers and 1 g/L for polymacromonomers. All polymer solutions were heated from 20 °C to 65 °C at very slow heating rates of 0,2 °C/min, while the exact temperature of the solution was monitored by an external sensor. Scanning wavelength was in range from 200 to 900 nm. All data to calculations were taken at λ = 400 nm.

Also *CMC* of macromonomers were determined by UV-VIS measurements. Aqueous solutions of macromonomers were prepared by dissolving the polymer and diluting to the desired concentration in the range of 0,0044 to 10 g/L. 25 μL of 0,4 mM DPH solution in methanol was added to the 2,5 mL of polymer solution, so that the final solution contained 1 % v/v methanol and 0,004 mM of DPH. The solutions were left in the dark to equilibrate for at least 1 h but no longer than 24 h. The spectroscopic measurements were made in the wave range 300-500 nm, where the main absorption intensity peak characteristic of DPH at 356 nm was used to estimation the cloud point of polymers.

6. Results and discussion

6.1. Preparation and characterization of poly(glycidol)-based macromonomers

The living anionic polymerisation of the oxiranes, phenyl glycidyl ether (GlPhE) and protected glycidol - glycidol acetal (GlAc), was used to synthesize the macromonomers. The polymerisation was carried out in dry THF at 60 °C using potassium *t*-butoxide as initiator and *p*-chloromethyl styrene as terminating agent. The protective acetal groups were removed under acidic conditions to give hydrophilic block of poly(glycidol).

6.1.1. Anionic polymerisation of glycidol acetal and phenyl glycidyl ether

As it is commonly known a polymerisation can be classified as *living* if it shows two characteristic features: linear increase of molecular weight with conversion as well as linear dependency of the $ln(M_0/M)$ vs. time. The occurrence of such features confirms that the concentration of the active centers in the system is constant (suppressed termination, fast initiation) and that the properties of the polymerisation products as M_n can be influenced. Additionally, under such conditions synthesis of block copolymers with targeted properties is possible. Thus, in order to confirm the *living* character of polymerisation of glycidol acetal and phenyl glycidyl ether kinetic measurements of the anionic polymerisation initiated with potassium *t*-butoxide were made.

Upon polymerisation samples were withdrawn at settled reaction times and analysed. Molecular weights of obtained poly(glycidol acetal)s were determined using *SEC-MALLS*, thus the absolute values of M_n were obtained. In case of poly(phenyl glycidyl ether) the *dn/dc* was not found in any available text books and M_n was not determined by *SEC-MALLS* measurements. However, on ^{1}H NMR spectrum the signals deriving from initiator moiety were well separated from the one deriving form polymer backbone. Taking into account that each polymer chain has in its structure *t*-butyl group, after removal of unreacted monomer, the *DP* of the samples were calculated using the intensity of one proton from the initiator signals.

The determination of the conversion of both monomers was made based on gas chromatography measurements using *p*-xylene as internal standard. The monomer conversion was determined according to the equation 6.1., where the monomer/*p*-xylene ratio was found from the peak area obtained from gas chromatography measurements.

$$\%conversion = \frac{M_0 - M_t}{M_0} \cdot 100\% \qquad \textbf{(6.1.)}$$

M_0 – initial concentration of monomer; ratio of monomer/*p*-xylene at t = 0

M_t – concentration of monomer at time t; ratio of monomer/*p*-xylene at any time of the reaction

In the block macromonomers the degree of the polymerisation of poly(glycidol) block should be 55, where only short block of poly(phenyl glycidyl ether) with *DP* about 10 will be introduced to the structure. Thus, the targeted degree of polymerisation of glycidol acetal upon kinetic measurements was 55, while in case of phenyl glycidyl ether lower value *DP* = 20 was chosen. The results are presented in Figure 6.1. and 6.2.

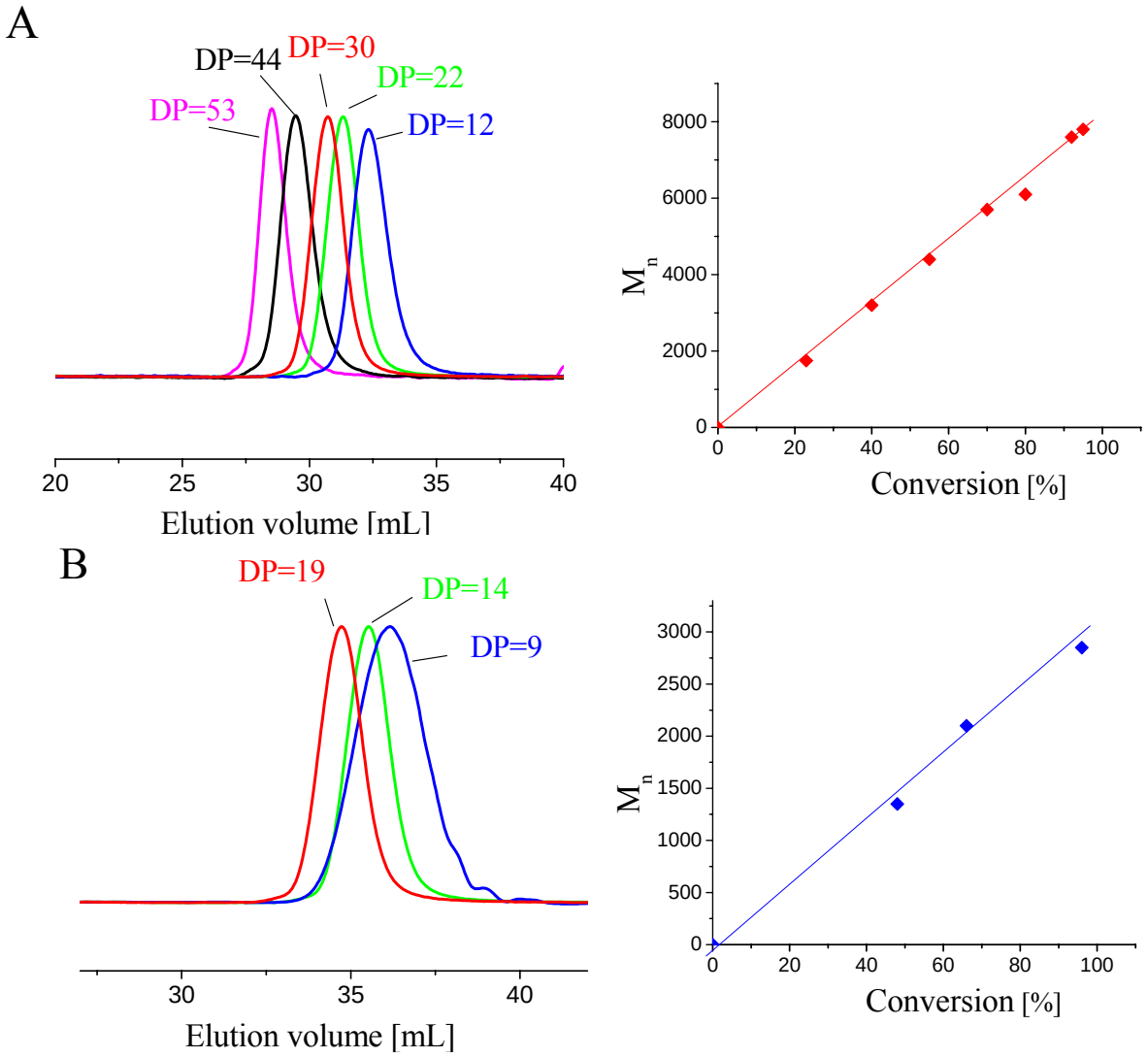


Figure 6.1. Molecular weight vs. conversion upon anionic polymerisation of glycidol acetal (A) and phenyl glycidyl ether (B); conversion determined by gas chromatography, M_n and *DP* calculated from *SEC-MALLS* (glycidol acetal) and ^{1}H NMR (phenyl glycidyl ether) measurements.

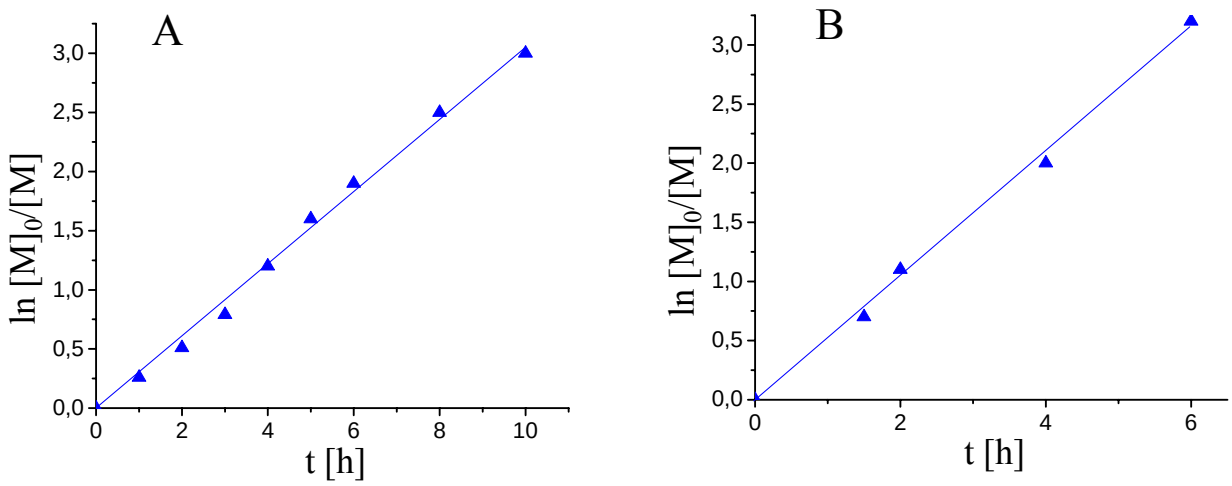


Figure 6.2. The dependence of $ln(M_0/M)$ vs. time upon anionic polymerisation of glycidol acetal (A) and phenyl glycidyl ether (B) based on gas chromatography.

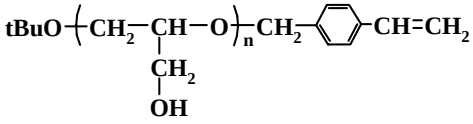
The living character of the polymerisation was confirmed. Under applied conditions desired *DP* of both polymers were obtained, where linear first order kinetic up to almost full conversion (Figure 6.2), as well as the linear increase of molecular weights with conversion (Figure 6.1) was obtained in both cases. The full conversion (above 99%) of glycidol acetal was obtained after 11 hours, while in case of phenyl glycidyl ether only 7 hours was necessary to reach that value.

SEC traces of all measured samples were monomodal and symmetrical without any additional shoulders, while the increase of the molecular weight was accompanied by the decrease of the elution volume. Additionally, *SEC-MALLS* analyses confirmed formation of narrow distributed poly(glycidol acetal)s with low polydispersity indices, where the dispersity index was decreasing with the increase of the molecular weight of the polymer.

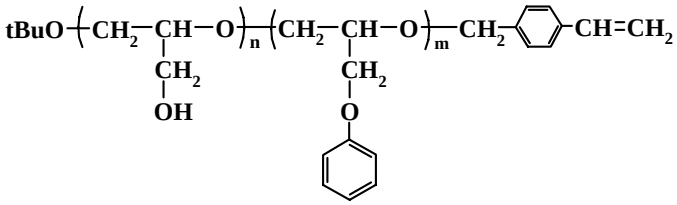
6.1.2. Synthesis of macromonomers

Based on the information collected upon kinetic measurements three types of amphiphilic macromonomers were obtained under controlled conditions:

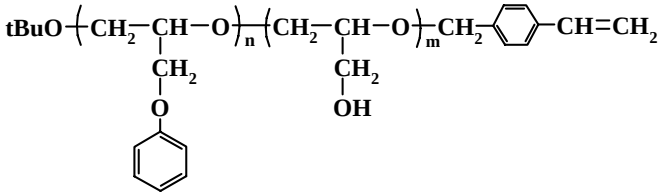
- α-t-butoxy-ω-vinylbenzyl-poly(glycidol) (PGl-St)



- Block macromonomer with the vinylbenzyl group attached to the hydrophobic block; *α-t*-butoxy-*ω*-vinylbenzyl-poly(glycidol)-*b*-poly(phenyl glycidyl ether) PGl-*b*-PGlPhE-St



- Block macromonomer with the vinylbenzyl group attached to the hydrophilic block *α-t*-butoxy-*ω*-vinylbenzyl-poly(phenyl glycidyl ether)-*b*-poly(glycidol) (PGlPhE-*b*-PGl-St)



The first step of macromonomer preparation included the anionic polymerisation of glycidol acetal or glycidol acetal and phenyl glycidyl ether followed by termination with *p*-chloromethyl styrene, where in case of block macromonomers the sequential monomer addition was applied. The *DP* of each macromonomer was varied by the monomer/initiator ratio in the reaction mixture. The structure of obtained macromonomers was confirmed by ^{1}H NMR measurements, where the example spectrum of block macromonomer PGlAc-*b*-PGlPhE and the assignments of peaks are shown in Figure 6.3.

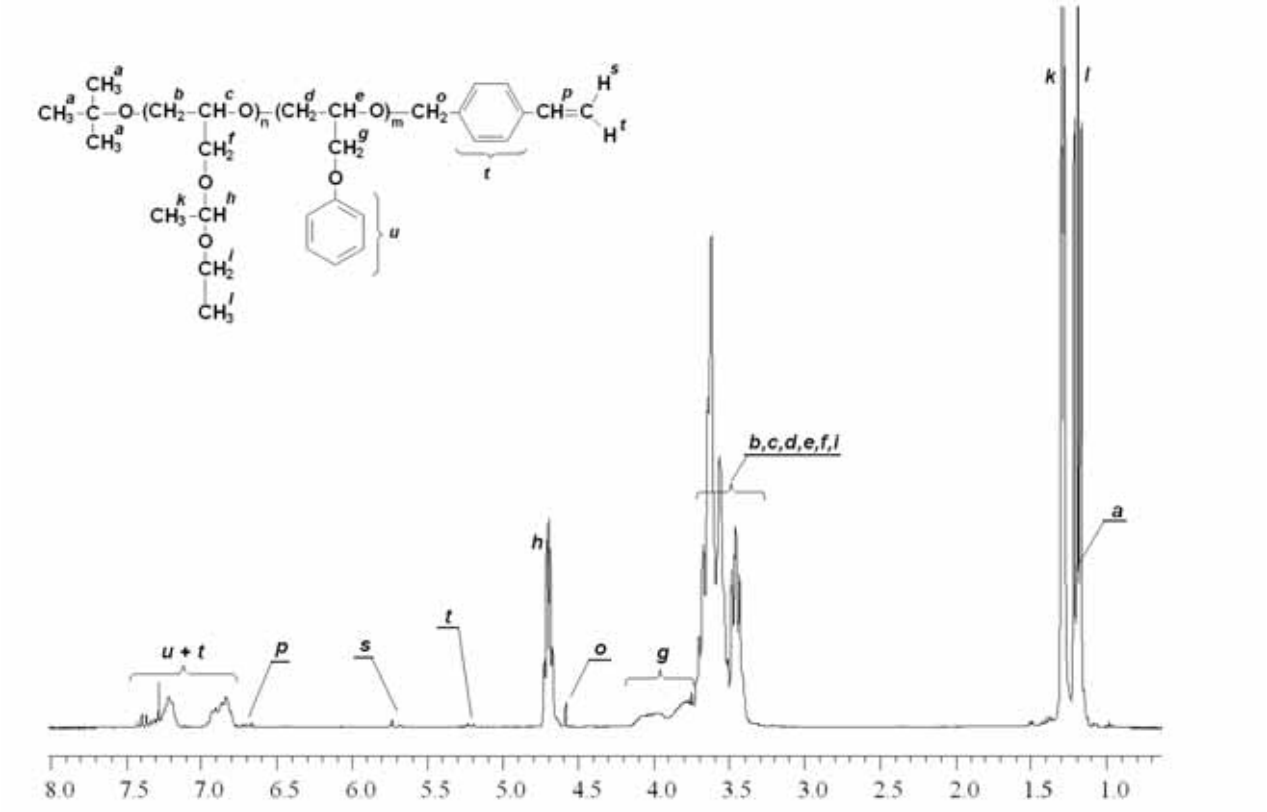


Figure 6.3. The ^{1}H NMR spectra of PGlAc-*b*-PGlPhE-St in $CDCl_3$.

It should be remembered that the excess of *p*-vinyl benzyl chloride was used in termination reaction. In the ^{1}H NMR spectra of macromonomer directly after termination two groups of signals were found: one deriving from attached vinyl benzyl groups and deriving from unreacted *p*-chloromethyl styrene. The successful purification of macromonomer from unreacted terminating agent was confirmed by disappearance of one group of signals as can be seen in Figure 6.4.

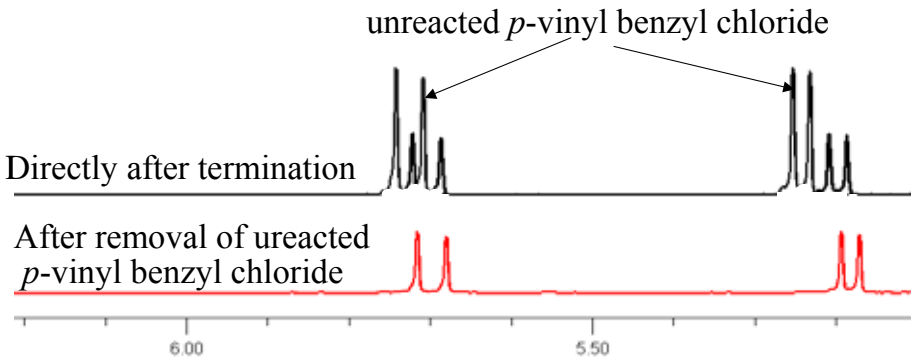


Figure 6.4. Part of ^{1}H NMR spectrum of poly(glycidol acetal) before (A) and after removal of unreacted *p*-vinyl benzyl chloride (B).

The compositions of obtained purified macromonomers calculated from ^{1}H NMR are presented at the next page in Table 6.1.

Additionally, synthesised macromonomers were characterised by *SEC-MALLS* measurements. The *SEC* traces of all synthesised macromonomers were monomodal. In case of block macromonomers the efficient, quantitive initiation of polymerisation of second monomer by the first block was observed, as no peak deriving from the first block was detected in the final product (directly after synthesis). The increase of molecular weight was accompanied by decrease of the elution volume as presented in Figure 6.5., more pronounced in case of PGlPhE-*b*-PGl. However, it was rather expected as the length of poly(phenyl glycidyl ether) block was much lower than of the corresponding poly(glycidol acetal) block.

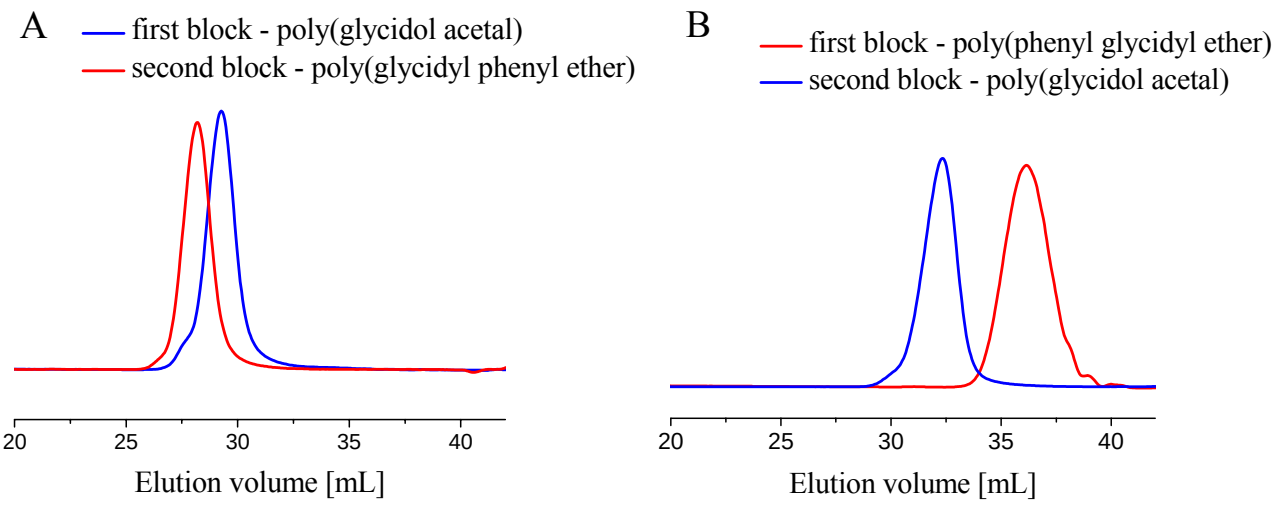


Figure 6.5. Synthesis of block macromonomers by sequential monomer addition: (A) polymerisation of glycidol acetal followed by polymerisation of phenyl glycidyl ether; (B) polymerisation of phenyl glycidyl ether followed by polymerisation of glycidol acetal.

The number average molecular weights and the dispersity indices (M_w/M_n) of obtained macromonomers calculated using the measured values of the refractive index increments (*dn/dc*), are summarized in Table 6.1.

Table 6.1. The molar masses of the synthesised macromonomers

Sample	Calculated from feed			From ^{1}H NMR (styrene end group)			From ^{1}H NMR (initiator end group)			From *SEC-MALLS*		
	n[a)]	m[b)]	M_n	n[a)]	m[b)]	M_n	n[a)]	m[b)]	M_n	M_n	M_w/M_n	*dn/dc*
$PGlAc_n$-St	40	-	6000	55	-	8100	-	-	-	7000[c)]	1,05	0,045
$PGlAc_n$-*b*-$PGlPhE_m$-St	60	8	10000	100	15	17000	-	-	-	10600[c)]	1,10	0,055
$PGlPhE_m$-*b*-$PGlAc_n$-St	52	7	8600	85	14	14700	-	-	-	9000[c)]	1,10	0,057
PGl_n-St[e)]	40	-	3200	60	-	4600	45	-	3600	4100[d)]	1,05	0,055
PGl_n-*b*-$PGlPhE_m$-St[e)]	60	8	5800	110	17	10800	66	10	6600	7200[d)]	1,10	0,065
$PGlPhE_m$-*b*-PGl_n-St[e)]	52	7	5000	95	14	9400	54	10	5700	6300[d)]	1,10	0,068

[a)] number average degree of polymerisation of poly(glycidol) or poly(glycidol acetal) block
[b)] number average degree of polymerisation of poly(phenyl glycidyl ether) block
[c)] solvent THF
[d)] solvent DMF
[e)] the symbols n and m in the sample name in the further work will be replaced with the proper values calculated from ^{1}H NMR using initiator group

The second step of macromonomer synthesis included acidic hydrolysis of protective acetal groups from poly(glycidol) segment. The ^{1}H NMR spectra of the hydrolysed polymers confirmed that the deprotection (removal of the protecting acetal groups) was quantitative. This was evidenced by the disappearance of the signal originating from the acetal groups, especially of two methyl groups in the region 1,0-1,4 ppm, where only a peak of initiator *t*-butyl groups is seen (Figure 6.6.).

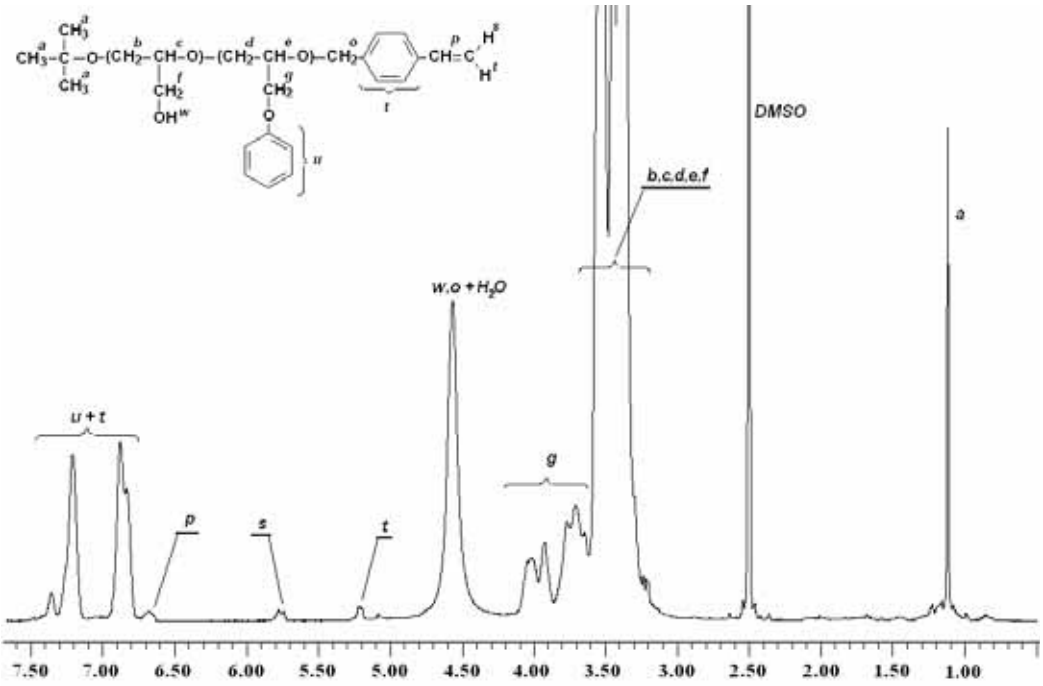


Figure 6.6. The ^{1}H NMR spectra of PGl-*b*-PGlPhE-St in DMSO-d_6.

In case of block copolymers the appearance of peaks from initiator and from end groups was different depending on the chemical surrounding, as can be seen in Figure 6.7. If the initiator group was attached to the poly(glycidol) block one sharp singlet was observed, while doublets deriving from terminator moiety were broad. In the opposite case, as the polymerisation of phenyl glycidyl ether was initiated by potassium *t*-butoxide, *t*-butyl group appeared as the multiplet (neighbourhood of benzyl group from monomer) whereas the doublets from terminator group were distinctly sharp. The signal deriving from both monomers building main chain were similar in all cases.

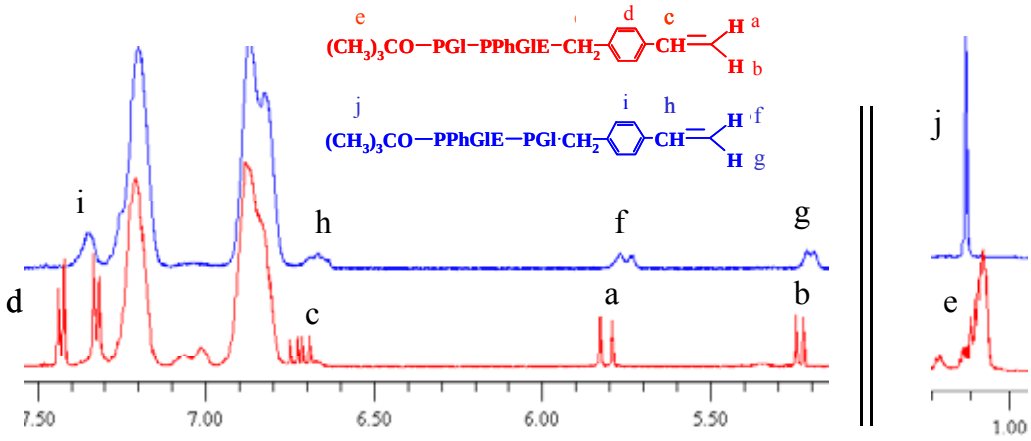


Figure 6.7. The parts of the spectra of PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St in DMSO-d_6.

The molecular weights before and after deprotection of acetal groups obtained from *SEC* measurements with the light scattering detection were little higher then expected. However, low molecular weights may be determined exactly if the refractive index increment and the sensitivity of the equipment used are high enough. For the obtained macromonomers values of the increment (0,055-0,068 mL/g) are relatively low (e.g. *dn/dc* for polystyrene is equal to 0,185 mL/g). Thus it is not sure if the sufficient scattering intensity was reached, what may increase the error of this method.

For the calculation of the compositions and molecular weights of the obtained macromonomers from ^{1}H NMR the intensity of the terminal protons of the vinyl benzyl end group was used. Obtained results for both protected and deprotected macromonomers presented in Table 6.1. are in all cases higher than those from *SEC-MALLS* measurements or calculated from the feed.

However, if the polymerisation system was perfectly living and the termination of the active centers quantitative, one would expect a good agreement between the molar masses measured from the end groups intensities in the ^{1}H NMR spectra and the values determined by *SEC* with absolute molar mass detection (*MALLS*). The lack of agreement suggests that some side reactions leading to not full functionality of macromonomers took place during their synthesis and the vinyl benzyl end group can not be used to calculate the molecular weight of macromonomers.

Therefore, the molecular weights and the compositions of obtained macromonomers were also calculated using the intensity of the initiator group signals in the NMR spectra. These results are in good agreement with values expected and measured by *SEC-MALLS* (Table 6.1.). The ratio of the intensity of one proton of end group and one proton of initiator group resulted in the degree of functionalisation of the poly(glycidol)-based macromonomers is presented in Table 6.2.

Table 6.2. The degree of functionalisation of the synthesised macromonomers

Sample	Degree of functionalisation [%]
PGl_n-St	59
PGl_n-*b*-$PGlPhE_m$-St	52
$PGlPhE_m$-*b*-PGl_n-St	53

As it can be seen the functionalisation of obtained deprotected macromonomers was not full and varied from 52 to 59 %. It means that only that amount of the polymer has the reactive vinyl benzyl group at the chain end. This will be confirmed by the results of the polymerisation of macromonomers experiments (see chapter 6.2.) Also the possible mechanism of the reactions causing decrease of the macromonomer functionality will be discussed later (see chapter 6.1.2.2.).

The same procedure can't be used for protected macromonomers because the signal of *t*-butyl group (incorporated initiator group (a)) overlaps with signals of two methyl units of the acetal groups (k+l) in the range from 1,0 to 1,4 ppm. Thus, calculation of degree of functionalisation is impossible.

6.1.2.1. *MALDI-TOF-MS* analysis of obtained macromonomers

As it was mentioned a convenient method allowing to check if the macromonomer is fully functionalized or is the mixture of non- and functionalized form is *MALDI-TOF-MS*. The example spectra are presented in Figure 6.8 and Figure 6.9.

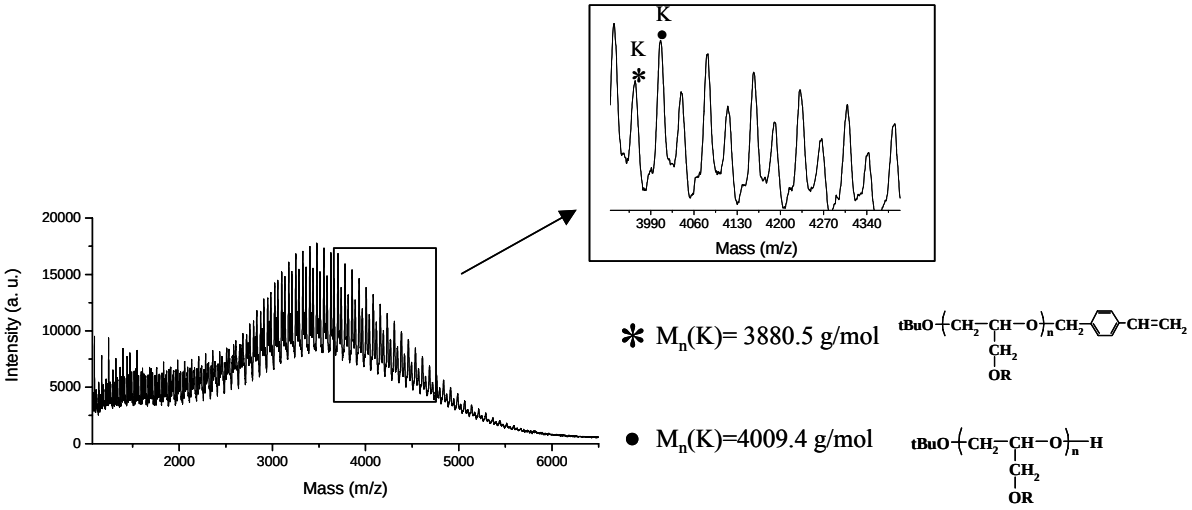


Figure 6.8. *MALDI-TOF-MS* spectra of macromonomer PGlAc-St before deprotection.

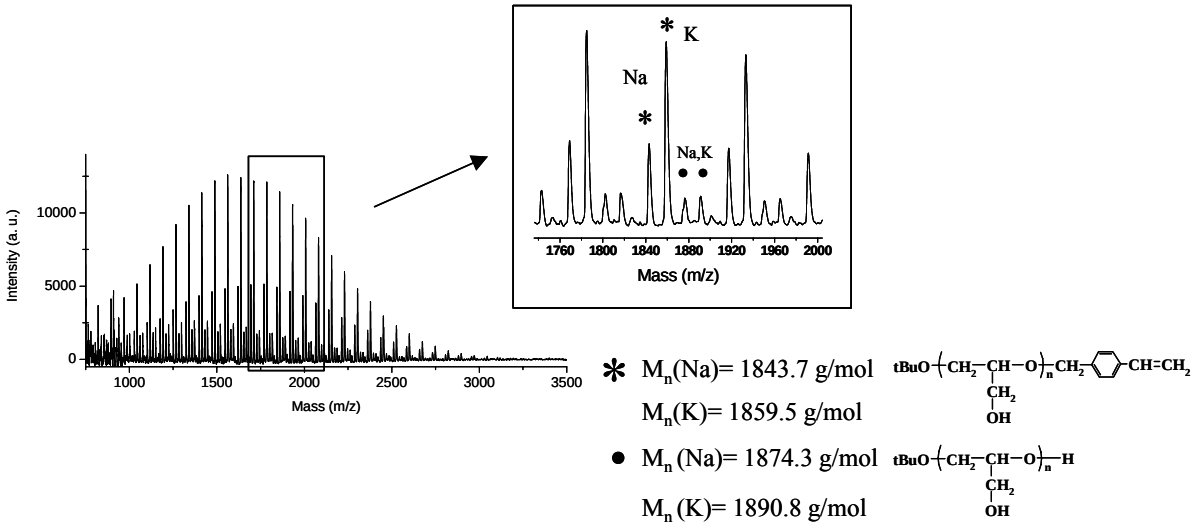


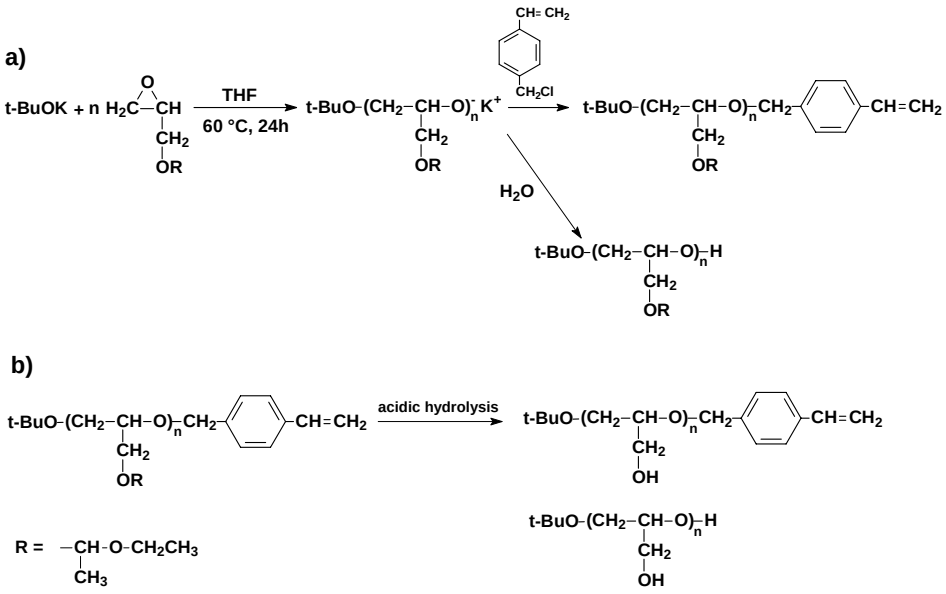
Figure 6.9. *MALDI-TOF-MS* spectra of macromonomer PGl-St (deprotected).

The end group analysis showed that all synthesized acetal macromonomers and deprotected glycidol macromonomers were a mixture of the macromonomer and the non-functionalized oligomer. Two different distributions were found in each spectrum. One distribution can be assigned to the macromonomer containing styrene reactive group (potassium or sodium adduct) and the second distribution originates from oligomers terminated with hydroxyl group

(potassium or sodium adduct). However, as it is not quantitive method the degree of functionalisation was not obtained. Nevertheless, not quantitive functionalisation of macromonomers was confirmed.

6.1.2.2. Optimisation of the macromonomer synthesis

Probable side reactions causing that the functionalisation of the macromonomers is not quantitive are presented in Scheme 6.1. One of them is the parallel termination of living chains with *p*-(chloromethyl) styrene and water during the termination step of the anionic polymerisation (route a)). Another possible side reaction may appear during the deprotection of the hydroxyl glycidol acetal group. Under acidic conditions hydrolysis of protecting acetal group appears accompanied by partial degradation of polyether chain causing cleavage of vinyl benzyl reactive group (route b)).



Scheme 6.1. Side reactions causing not full functionalisation of macromonomers:
a) not efficient termination of living chains with p-(chloromethyl)styrene
b) partial hydrolysis of the ether linkage of vinyl benzyl group during hydrolysis of acetal protecting groups of glycidol.

Because *MALDI-TOF-MS* measurements do not quantitatively reflect the amount of species giving rise to the individual signals, the ratio between functionalized macromonomer and oligomer can not be calculated from these measurements. However, taking into account the results obtained from ^{1}H NMR (Table 6.1.) the prevailing side reaction seems to be not quantitive termination of living chains with *p*-vinyl benzyl chloride (significant difference between the molecular weights of the macromonomer calculated from feed and obtained from

^{1}H NMR when vinyl benzyl end group protons were used and the good agreement between the molecular weights calculated from feed and measured by *SEC-MALLS*). The second side reaction is probably less important, although it can not be neglected.

The affords were then focused on the improvement of the introduction of the vinylbenzyl end group into the polymer chain. The first attempts included the application of the higher excess of terminating agent up to ten-molar excess referred to the amount of active sides. This led to district improvement of degree of functionalisation up to about 70 – 74 %, however still not full functionalisation of macromonomers was observed (Table 6.3.). The further increase of the amount of the terminating agent did not improve the results.

Table 6.3. The molecular weights of the synthesised macromonomers

Sample	Calculated from feed			From ^{1}H NMR (styrene end group)			From ^{1}H NMR (initiator group)			^{1}H NMR	From *SEC-MALLS*	
	n[a)]	m[b)]	M_n	n[a)]	m[b)]	M_n	n[a)]	m[b)]	M_n	$DF^{e)}$	M_n	M_w/M_n
$PglAc_n$-St	30	-	4600	42	-	4600	-	-	-	73	4700[c)]	1,02
PGl-St	30	-	2400	43	-	3200	32	-	2550		2500	1,02
$PglAc_n$-St	55	-	8200	80	-	11700	-	-	-	71	8200[c)]	1,06
PGl-St	55	-	4200	80	-	5800	57	-	4400		4500	1,06
$PGlAc_n$-*b*-$PGlPhE_m$-St	55	8	9400	69	9	11600	-	-	-	65	9000	1,05
PGl_n-*b*-$PGlPhE_m$-St	55	8	5500	70	9	6500	46	6	4500		5000	1,05
$PGlAc_n$-*b*-$PGlPhE_m$-St	55	8	9400	80	11	13200	-	-	-	65	9500	1,07
PGl_n-*b*-$PGlPhE_m$-St	55	8	5500	79	11	7500	52	8	5300		5900	1,07
$PGlAc_n$-*b*-$PGlPhE_m$-St	55	8	9400	77	10	12800	-	-	-	68	9300	1,03
PGl_n-*b*-$PGlPhE_m$-St	55	8	5500	76	10	7200	53	8	5500		6400	1,02
$PGlPhE_m$-*b*-$PGlAc_n$-St	55	8	9400	70	11	11900	-	-	-	74	9500	1,06
$PGlPhE_m$-*b*-PGl_n-St	55	8	5500	70	11	6800	52	8	5300		5700	1,06
$PGlPhE_m$-*b*-$PGlAc_n$-St	55	8	9400	75	11	12600	-	-	-	72	10000	1,05
$PGlPhE_m$-*b*-PGl_n-St	55	8	5500	75	11	7200	54	9	5500		6000	1,05
$PGlPhE_m$-*b*-$PGlAc_n$-St	55	8	9400	71	10	12100	-	-	-	74	9600	1,05
$PGlPhE_m$-*b*-PGl_n-St	55	8	5500	71	11	6900	53	8	5500		6000	1,05

[a)] number average degree of polymerisation of poly(glycidol) or poly(glycidol acetal) block
[b)] number average degree of polymerisation of poly(phenyl glycidyl ether) block
[c)] solvent THF
[d)] solvent DMF
[e)] degree of functionalisation calculated from the ratio of intensity of one proton calculated from end group and initiator group

As it was presented in the literature review, the reactivity of the macroanion depends on counterions which are used for the neutralization of the growing polymer chains. As potassium *t*-butoxide was used as initiator the potassium counterion neutralizes the anionic growing centre during termination with *p*-(chloromethyl)styrene. However, it is a relatively large ion and it was expected that it may make the termination of the living chain difficult. Thus, the second idea included the change of the counterion from large potassium to smaller sodium. As presented in Scheme 5.3 the two step synthesis involved the preparation of the poly(glycidol acetal) by anionic polymerisation in the previously described method and termination of the living chain with water. As next the *ω*-hydroxyl end group of obtained polymer was modified using sodium hydride and *p*-(chloromethyl)styrene according to Wiliamson's reaction. The spectra of the glycidol acetal terminated with water and of obtained macromonomer is presented in Figure 6.7.

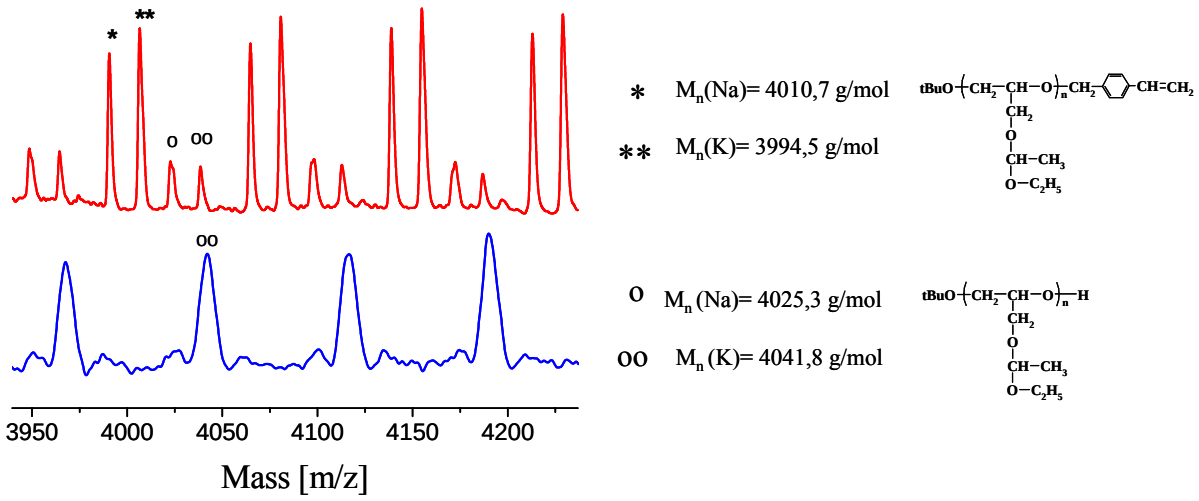


Figure 6.10. Part of the *MALDI-TOF-MS* of macromonomer obtained according to Wiliamson`s synthesis PGl_{55}-St .

As it can be seen the mixture of functionalized macromonomer and un-functionalized oligomer was obtained. The functionalisation of macromonomer calculated according to ^1H NMR was on the level of 70 %. Thus, the change of the cation did not improve the results.

The problems of non-quantitive introduction of the reactive group to the poly(glycidol acetal) was not solved.

In the further work the composition of all macromonomers will be referred to the values calculated from the ^1H NMR using intensity of the initiator group for example PGl_{55}-*b*-$PGlPhE_8$-St.

6.1.3. Thermal properties of obtained macromonomers

The thermal properties of all obtained macromonomers were investigated using differential scanning calorimetry. T_g of low molar mass poly(glycidol)s, poly(glycidol acetal)s and poly(phenyl glycidyl ether)s (molecular weight below 7 000 g/mol) have not been reported so far. Thus, first the thermograms of this polymers with the molecular weights similar to the corresponding blocks in macromonomer structure were investigated. The results are presented in Table 6.4. and in Figure 6.8.

Table 6.4. T_g of low molecular weight polymers

Sample	T_g [°C]
PGlAc (M_n = 9800 g/mol)	- 64
PGl (M_n= 5000 g/mol)	- 60
PGlPhE (M_n = 1800 g/mol)	8

As it can be seen all measured polymers show low T_g values and at room temperature are in rubber state. However, as poly(phenyl glycidyl ether) shows T_g higher as poly(glycidol acetal) or poly(glycidol) it was expected that the introduction of the hydrophobic spacer to the macromonomers structure will increase their T_g.

The thermal properties of both the macromonomers before and after removal of the protecting acetal groups were investigated in the range –80 to 25 °C. In the investigated range all the macromonomers showed a single T_g as can be seen in Figure 6.8. In case of PGl-St and PGlAc-St the obtained T_g values were similar to the one found for the corresponding homopolymers with similar molecular weights. For block macromonomers the introduction of hydrophobic spacer of poly(phenyl glycidyl ether) to the structure led to the increase of the T_g., however probably because the hydrophobic block was short only one transition was observed. The T_g values are presented in Table 6.5.

Table 6.5. T_g of macromonomers before and after removal of acetal groups.

Sample	T_g [°C]	Sample	T_g [°C]
$PGlAc_{45}$-St	- 64	PGl_{45}-St	- 60
$PGlAc_{66}$-*b*-$PGlPhE_{10}$-St	- 55	PGl_{66}-*b*-$PGlPhE_{10}$-St	- 44
$PGlPhE_{10}$-*b*-$PglAc_{54}$-St	- 56	$PGlPhE_{54}$-*b*-PGl_{10}-St	- 32

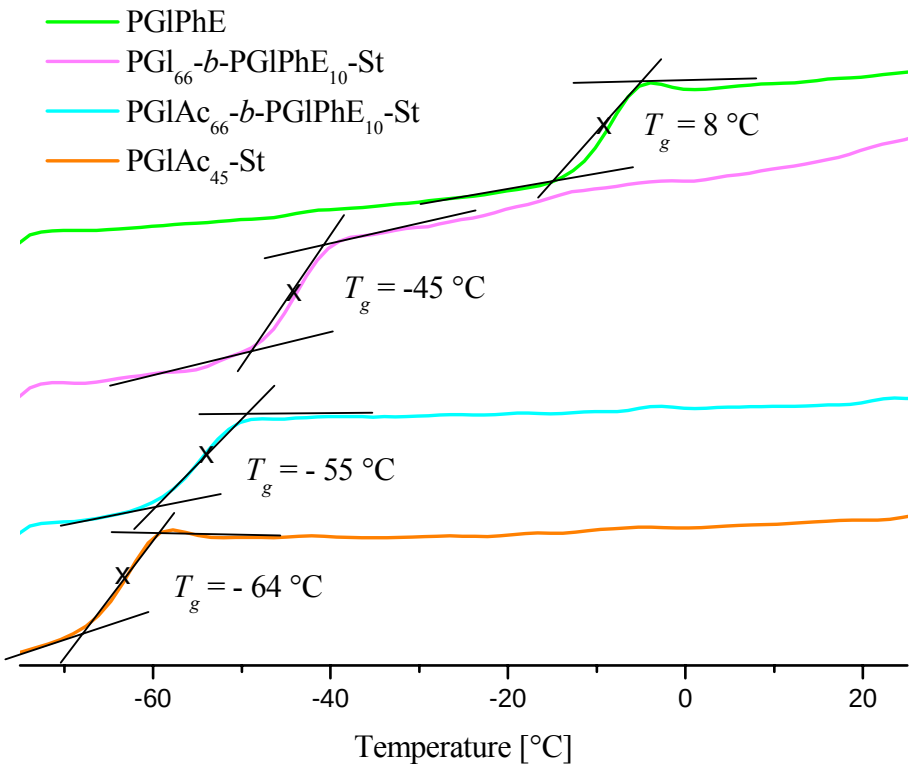


Figure 6.11. The example thermograms of synthesised macromonomers.

6.1.4. Amphiphilic properties of macromonomers

Poly(glycidol acetal) and poly(phenyl glycidyl ether) are soluble in a wide range of solvents such as chloroform, THF, acetone, benzene, DMF, DMSO, while poly(glycidol) is a highly hydrophilic polymer soluble only in polar solvents like water, low alcohols, DMF or DMSO. Thus, in case of block macromonomers of PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St the solubility of both block is completely different where common solvents are only DMF and DMSO. However, this block macromonomers showed amphiphilic properties and were soluble in the solvents of both blocks, what was not expected as only short hydrophobic blocks were introduced to the polymer structure.

The unique solution and associative properties of amphiphilic polymers are the consequence of their molecular structure. In fact when a block copolymer is dissolved in a liquid that is a thermodynamical good solvent for one block and a precipitant for the other, the copolymer chains may associate reversibility to form micellar aggregates which resemble in most of their aspects to those obtained with classical low molecular surfactants. The micelle consist of more or less swollen core of the insoluble blocks surrounded by a flexible fringe of soluble blocks. As ^{1}H NMR provides the information about local segmental mobility it can be used to

show the amphiphilic properties of block macromonomers [48], where such data are complementary to structure of the polymer in the solution.

By simple switching of the solvent from good for both blocks (DMSO) to selective, i.e. good one only for poly(glycidol) block (water), or poly(phenyl glycidyl ether) (chloroform) the different spectra were observed. In DMSO signals from both blocks are well visible where in water, non solvent for poly(phenyl glycidyl ether) block, the signals from poly(glycidol) are sharp and district, while the one from hydrophobic spacer are only slightly visible as it can be seen in Figure 6.12. In chloroform the situation is opposite as the signals from poly(glycidol) are significantly suppressed (decrease of the value of integral) and this time insoluble poly(glycidol) blocks form core surrounded by poly(phenyl glycidyl ether) soluble in chloroform short chains. However, as the signals of the polyether groups forming main chain from poly(glycidol) and poly(phenyl glycidyl ether) are overlapping disappearance of poly(glycidol) peaks in chloroform is not good visible. However, the peak from hydroxyl group disappears completely. In DMSO as it was already presented signals of both blocks are well visible.

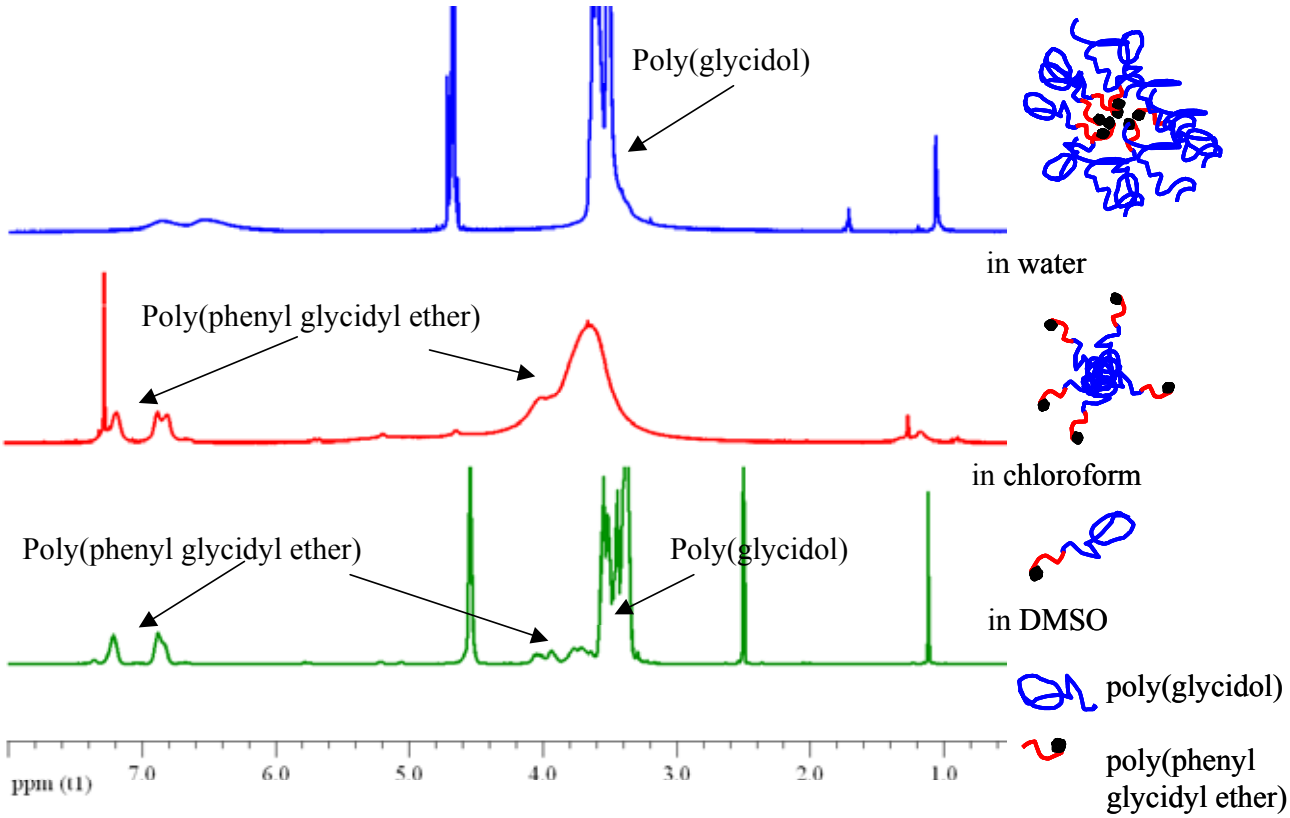


Figure 6.12. The spectra of PGl_{66}-*b*-$PGlPhE_{10}$-St in deuterated water, chloroform and DMSO.

6.1.5. Critical micellization concentration *(CMC)*

A number of amphiphilic block copolymers was shown to aggregate in the form of micelles in water [110]. As it was shown during ^{1}H NMR analysis the obtained block macromonomers show amphiphilic properties thus are expected to form micelles. However, taking into account that PGl-St macromonomer is bearing the hydrophobic vinyl benzyl group it is expected that it will also form some organised structures in water.

Three different methods were used to the estimation of critical micellization concentration of studied macromonomers in water: *UV-VIS*, surface tension and static light scattering, where each of the techniques used different feature of micelles.

6.1.5.1. *CMC* by UV-VIS

Spectroscopic techniques, based either on optical absorption or on emission of light from probe molecule , are now well-established for investigating a wide range of physical properties of micellar solutions [242-243]. The fact that micelles can solubilize relatively large amounts of sparingly water-soluble compounds has been used to determine the onset of micelles formation by measuring the concentration of a chosen sparingly soluble substance, possessing a convenient *UV-VIS* absorbing chromophore, in the presence of increasing amounts of polymer able to form micelles. Below the *CMC*, the concentration of the solubilizate in the solution is the same as in aqueous solution in the absence of surfactant. Above *CMC*, the total amount of additives in solution increases sharply as the total micelle concentration increases.

In this work the solubilization of a dye (1,6-diphenyl-1,3,5-hexatriene, *DPH*) in aqueous solution of investigated macromonomers, detected by *UV-VIS* spectra, was employed in the investigation for the determination of the *CMC* values of macromonomers. The fluorescence efficiency of *DPH* is zero in a hydrophilic environment and increases in a hydrophobic environment, such as the core of the micelle formed in water, thus providing a sensitive indicator of micelle formation with increasing concentration. The example curves of *DPH* adsorption intensity at 356 nm vs. log C are presented in Figure 6.13.

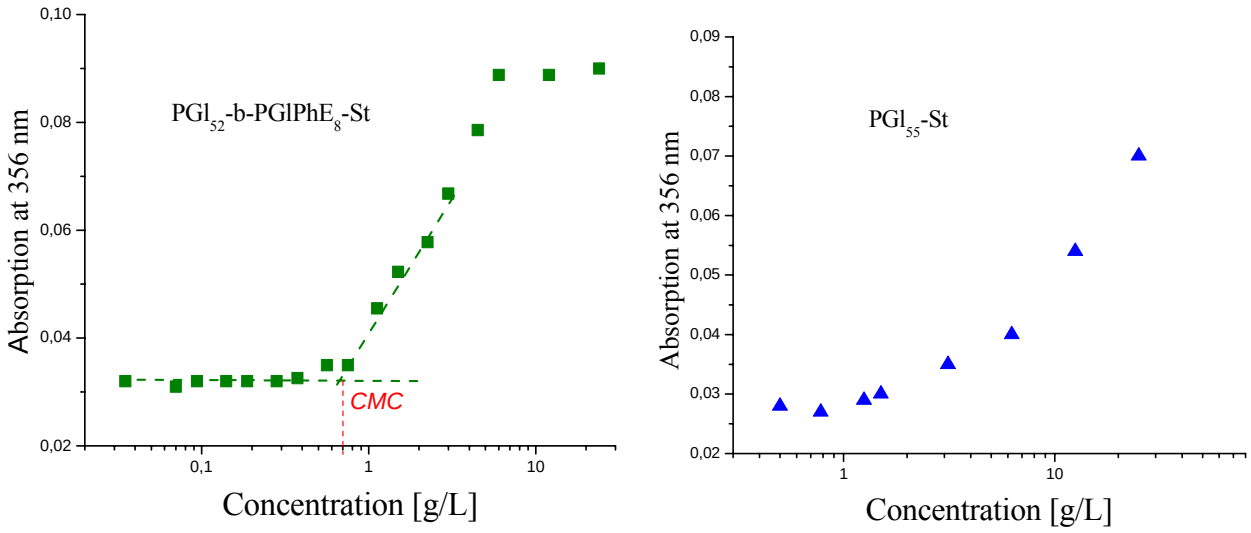


Figure 6.13. Detection of *CMC* by *UV-VIS* measurements.

The curves obtained during measurements of block macromonomers were sigmoidal, with the district increase of the absorption above certain concentration. The first inflection of the curve indicates the micelles formation and was used to the determination of the *CMC* of investigated macromonomers gathered in Table 6.6. The second inflection corresponds to the complete solubilization of the dye in formed micelles.

Table 6.6. *CMC* by *UV-VIS* measurements.

Sample	*CMC* [g/L]
PGl_{55}-St	not found
PGl_{52}-*b*-$PGlPhE_8$-St	0,8
$PGlPhE_9$-*b*-PGl_{54}-St	0,6

In case of PGl-St macromonomers determination of the precise value of *CMC* using this method was problematic. Although increase of the concentration of the polymer was accompanied by the increase of the absorbance no district inflection was noticed at the curve. However, the only hydrophobic part of this macromonomers are end groups vinylbenzyl and *t*-butyl. Even if both of them are involved in formation of the core of the micelle it is much smaller then the one formed in case of block macromonomers. The smaller amounts of the *DPH* can solute in such micelles core, what make the detection of *CMC* by this method complicated.

6.1.5.2. *CMC* by surface tension

Adsorption of the surface active-agent such as amphiphilic macromonomers causes a reduction in the surface tension at the air/water interface. This compounds are effective in reducing the surface tension of an aqueous solution, what is consistent with the effective positive adsorption at an air/water interface.

Figure 6.14. represents semi logarithmic plots of surface tension of aqueous macromonomer solution with the concentration. As it can be seen with increasing macromonomer concentration the surface tension decreases almost linearly and becomes constant above a certain concentration. The break point observed for both these macromonomers implies subsequent aggregation and may correspond to the *CMC*.

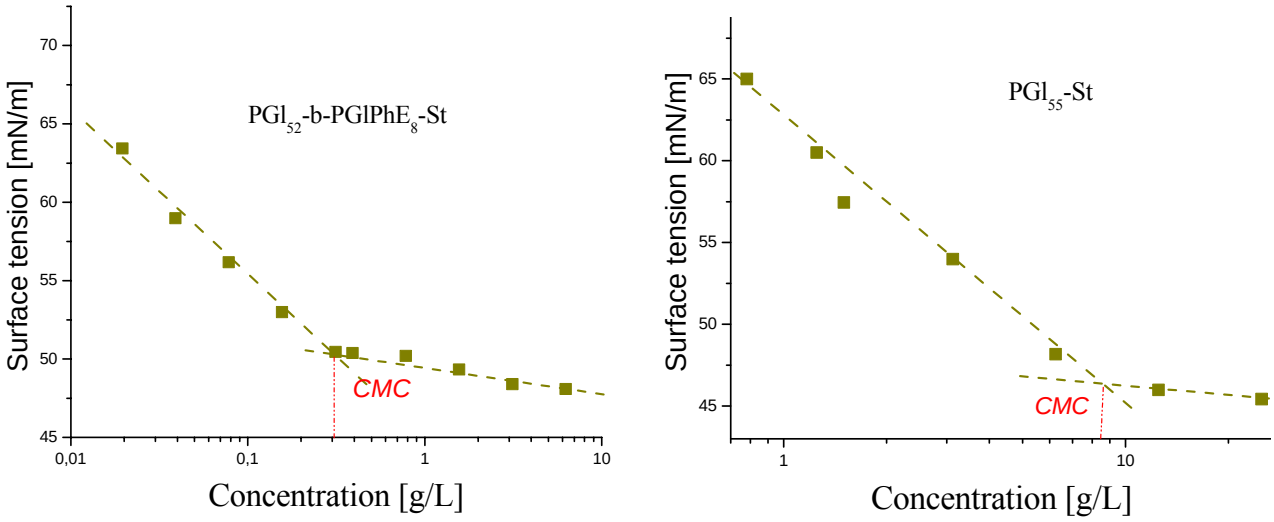


Figure 6.14. *CMC* by surface tension.

The surface tension curves for these amphiphiles suffered a downward trend after the break point. However, such behaviour was already observed and was assigned to the polydispersity of amphiphiles [134]. Nevertheless, there could be another possibility too. The aggregation process for these macromonomers are cooperative in nature and continue throughout the concentration range studied.

The *CMC* values determined from the inflection point are collected in Table 6.7. The *CMC* obtained by *UV-VIS* were slightly higher than that obtained from surface tension method. However, this is a common feature for non-ionic surfactant with very low *CMC* [244]. When

CMC is low at a surfactant concentration just above the *CMC*, the micellar population will be low and the amount of the probe solubilized in the micelles will be too little to be detected.

Table 6.7. *CMC* values of macromonomers according to surface tension measurements.

Sample	*CMC* [g/L]
PGl_{55}-St	8,5
PGl_{52}-*b*-$PGlPhE_8$-St	0,75
$PGlPhE_9$-*b*-PGl_{54}-St	0,6

6.1.5.3. *CMC* by static light scattering

The *CMC* was also determined by static light scattering experiment at 25 °C, where the Rayleigh ratio of aqueous and DMF macromonomer solution at scattered angle of 90° was plotted against the concentration. Figure 6.15. clearly proved the micelle formation in water as the R_{90} increased steeply with a concentration above that to be identified as *CMC*. From the other side in DMF which is a good solvent for both blocks only negligible scattering was observed indicating the molecular dissolution of the same polymer.

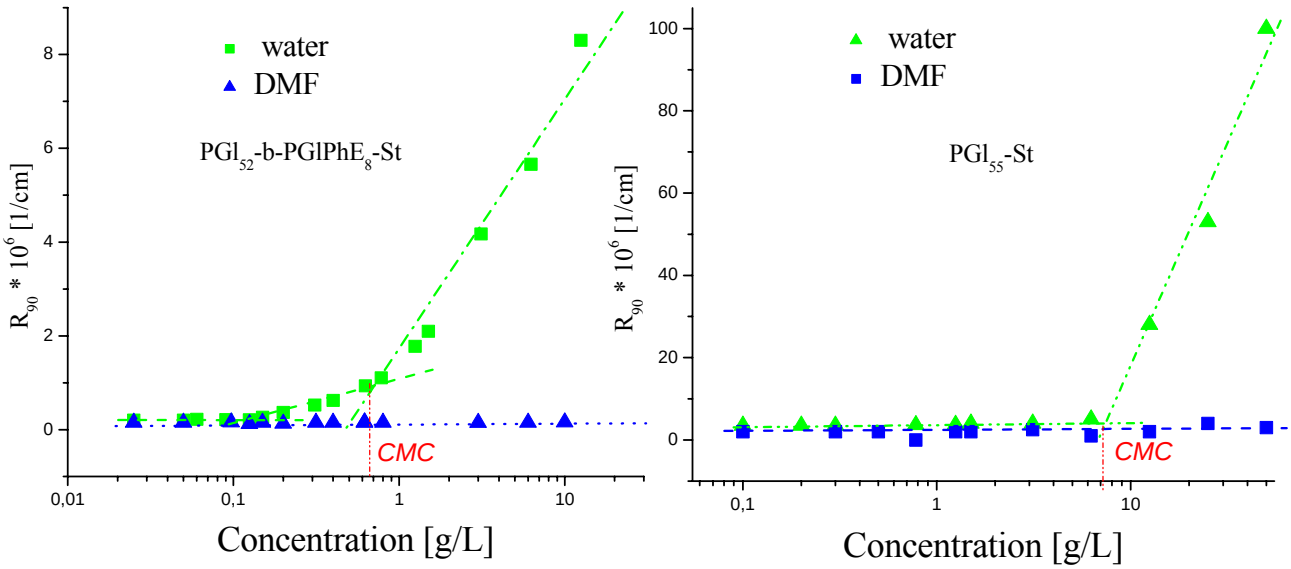


Figure 6.15. Detection of *CMC* by static light scattering measurements.

In case of aqueous solution of block copolymers the two step increase of R_{90} was observed. However, such behaviour can be explained in terms of *premicelles* formation described in the literature review [23]. As light scattering methods detects any organization of the molecules in

the solution the slight increase of the R_{90} for PGl-*b*-PGlPhE-St in the concentration region from 0,1 to 0,8 g/L indicates probably the formation of loose aggregates and the initiation of micellization. The concentration of the polymer is too low so that well-defined micelles could not be formed. However, starting from the concentration 0,8 g/L, which was identified as *CMC* the district increase of R_{90} with increase of concentration indicates formation of well-organized micelles.

The *CMC* of investigated macromonomers were determined according to the method presented in Figure 6.14. and are presented in Table 6.8. Taking into account the data obtained by *UV-VIS* or surface tension measurements the accepted way of interpretation of the data seems to be correct.

Table 6.8. *CMC* values of macromonomers according to *SLS*.

Sample	*CMC* [g/L]
PGl_{55}-St	9,0
PGl_{52}-*b*-$PGlPhE_8$-St	0,75
$PGlPhE_9$-*b*-PGl_{54}-St	0,6

To conclude, the *CMC* values obtained from the used methods were similar. For the block macromonomers bearing the hydrophobic spacer the *CMC* was low and varied in the range 0,3-0,8 g/L. The macromonomers bearing *p*-vinylbenzyl group as the only hydrophobic groups showed much higher *CMC* at the range 9-10 g/L.

6.1.6. Light scattering measurements of the aggregation of the macromonomers

The micellization behaviour of hydrophobic-hydrophilic moieties has been studied extensively in aqueous medium, where only little attention has been paid to their self-aggregation in non-aqueous solvents. Thus, the micellization of all type of poly(glycidol)-based macromonomers in water as well as aggregation of poly(glycidol)-based block macromonomers in THF was studied by light scattering techniques. This way is more direct than many other methods described in the literature and is free of any choice of thermodynamic model.

6.1.6.1. Dynamic light scattering measurements in water

The formation of micelles by all studied macromonomers was confirmed, however different results were obtained for block macromonomers in comparison to PGl_{55}-St.

In case of PGl_{55}-St bimodal distribution of the hydrodynamic radius was observed. The formed micelles were relatively large with the size of 51 nm, while the second peak at 1,5 nm corresponded to the polymer (unimer) not involved in formation of micelles. It is possible that the unimer remained in the dynamic equilibrium with the micellar structure. However, it should be remembered that all the studied samples are the mixture of functionalized macromonomers and not functionalized oligomer. In the lack of polymerising *p*-vinyl benzyl group the only hydrophobic group in the oligomer structure is the *t*-butyl group from the initiator of the anionic polymerisation. However, it is too less hydrophobic so that could be involved in formation of micelles. As the result the oligomers remain molecularly soluble. The structure of obtained micelle for PGl-St was then proposed as presented in Figure 6.16.

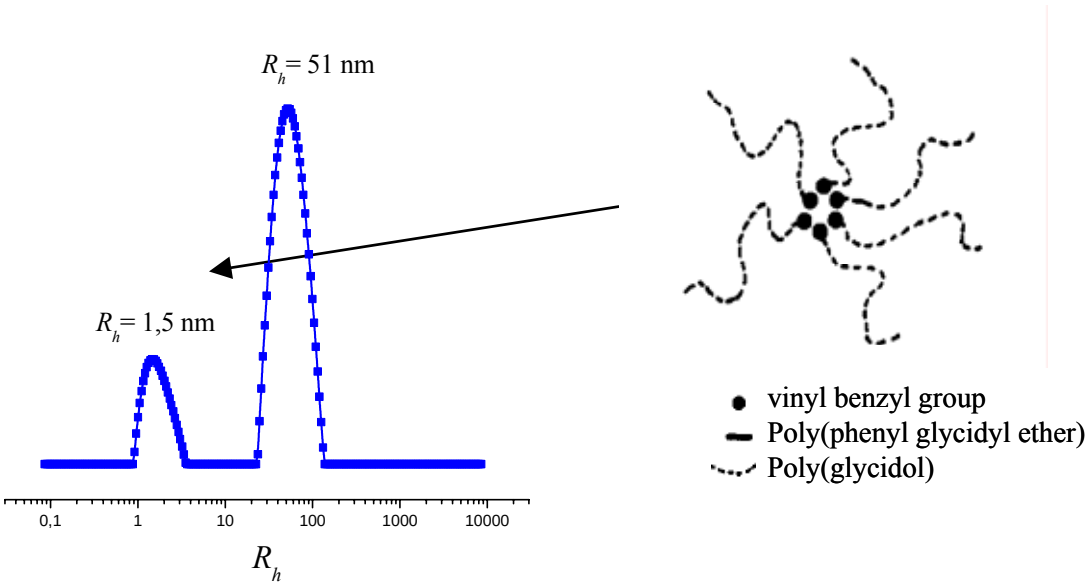


Figure 6.16. The micelles of PGl_{55}-St in water, c = 20 g/L.

In case of block macromonomers monomodal distribution and much more compact micelles were formed with the hydrodynamic radius in the range of 10 nm (Figure 6.17.). As the R_h measured at different angels were the same within experimental error it can be concluded that the formed micelles are relatively monodisperse. In the studied range the R_h was independent on the concentration (from 0,8 to 5 g/L).

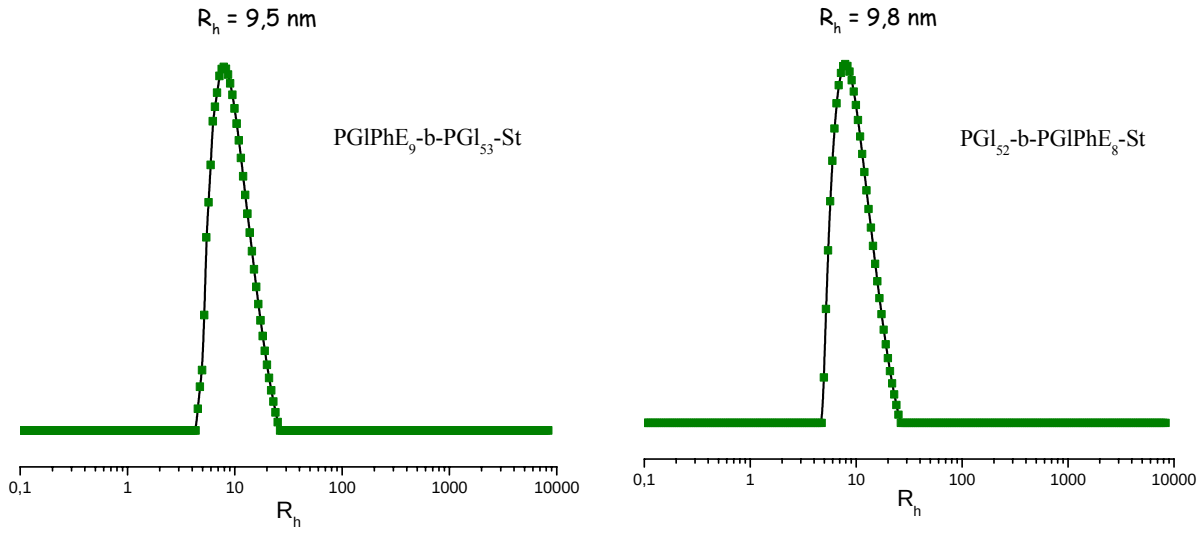


Figure 6.17. The micelles formed by $PGlPhE_9$-*b*-PGl_{54}-St and PGl_{52}-*b*-$PGlPhE_8$-St in water, C = 5 g/L.

Taking into account the data obtained from *DLS* measurements the structure of the micelle can be presented as in Figure 6.18. As the size of the micelle is the same in case of PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St the formation of loop by poly(glycidol) chain is probably not obtained because the length of its chain is too low to form the loop. From the other side it can not be excluded that loops are formed, however, because of not quantitive functionality of macromonomers only about a half of the chains is able to their formation. The oligomers without the hydrophobic end group remain stretched, what increase the R_h of the whole micelle.

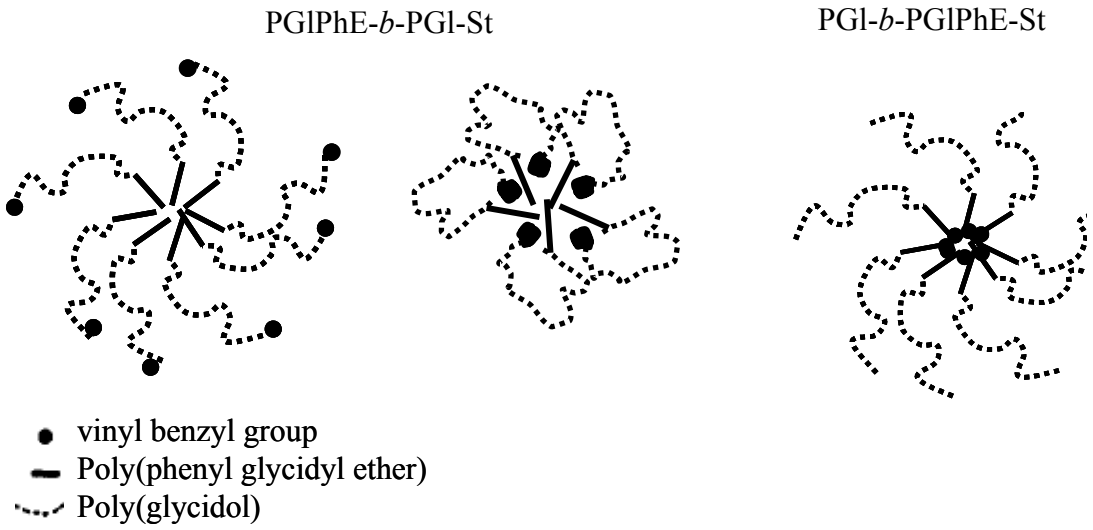


Figure 6.18. The structure of micelles formed by block macromonomers in water.

6.1.6.2. Static light scattering measurements - number of aggregation in water

The aggregation number of macromonomers in micelles is very important in the terms of their polymerisation since average number of the molecules per unit corresponds to that of the double bonds and of *ω*-alkyl groups of the macromonomers. Thus, from the concentration and angular extrapolations of the excess integrated scattered intensity of the copolymer samples in dilute aqueous solutions, i.e. from the Zimm plots the apparent molecular weight of micelles were obtained. When the values of the refractive index increments of the corresponding polymers were used the weight-average molecular weights (M_w) and the corresponding average association numbers could be computed. The results are listed in Table 6.9.

Table 6.9. Parameters of macromonomers in water according to *SLS*.

Sample	*dn/dc* in water	M_n in DMF [g/mol]	M_w of micelle [g/mol]	*N*
PGl_{52}-*b*-$PGlPhE_8$-St	0,134	5900	582 000	116
$PGlPhE_9$-*b*-PGl_{54}-St	0,136	6000	486 000	81

As it can be seen the investigated macromonomers showed different aggregation numbers. In case of $PGlPhE_9$-*b*-PGl_{54}-St the obtained value was lower then for the macromonomer of similar length of block, but opposite order of the blocks (double bond attached to the hydrophobic block). It is possible that the differences are connected with the structures of formed micelles. In case of $PGlPhE_9$-*b*-PGl_{54}-St the vinyl benzyl groups may form core of the micelle too. That increase the hydrophobicity of the core of micelle and may lead to the decrease of the amount of chains forming the core.

Estimation of M_w of micelles formed by PGl-St by SLS was not performed. As this polymer showed bimodal distribution upon *DLS* measurements the determined M_w would be in that case the average value between molecular weight of micelles and polymer, thus not correct.

6.1.6.3. Dynamic and static light scattering measurements in THF

Dynamic light scattering measurements of behaviour of block macromonomers were also preformed in THF, which is a solvent of poly(phenyl glycidyl ether) block but non-solvent for poly(glycidol) block. The results are presented in Figure 6.19.

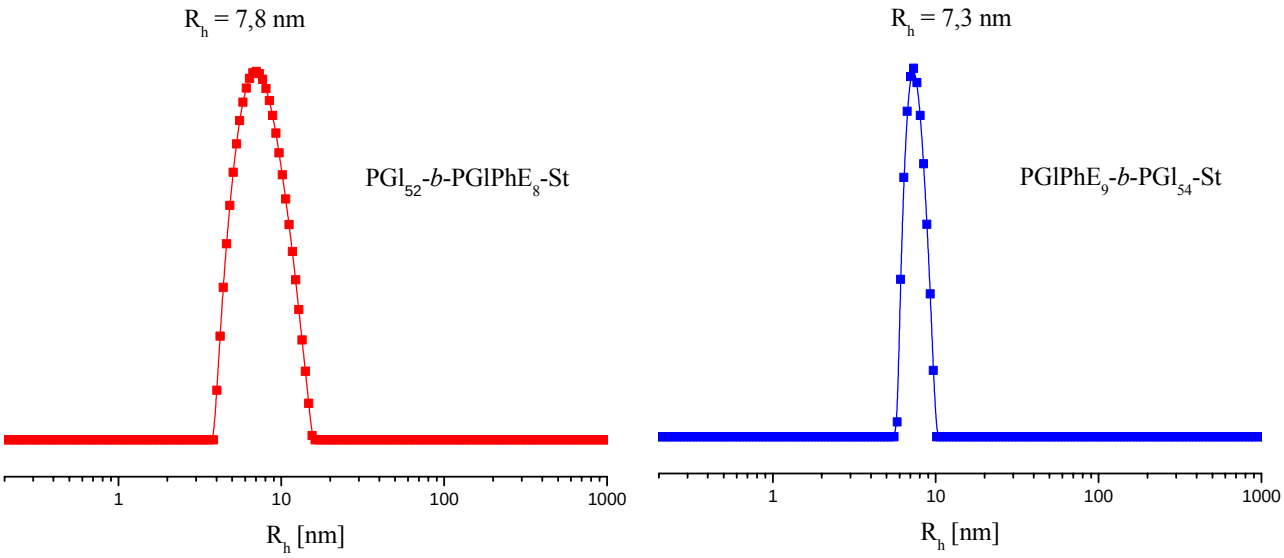


Figure 6.19. The micelles formed by $PGlPhE_9$-*b*-PGl_{54}-St and PGl_{52}-*b*-$PGlPhE_8$-St in THF, C = 5 g/L.

Formation of small well-defined narrow distributed micelles in case of both investigated macromonomers was observed. However, in that solvent the formation of opposite micelles is observed, where poly(glycidol) forms insoluble core surrounded with soluble in that solvent poly(phenyl glycidyl ether) chains as presented in Figure 6.20. As vinyl benzyl groups attached to poly(glycidol) chain are soluble in THF it is also possible for $PGlPhE_9$-*b*-PGl_{54}-St that they are concentrated on the border of core and shell.

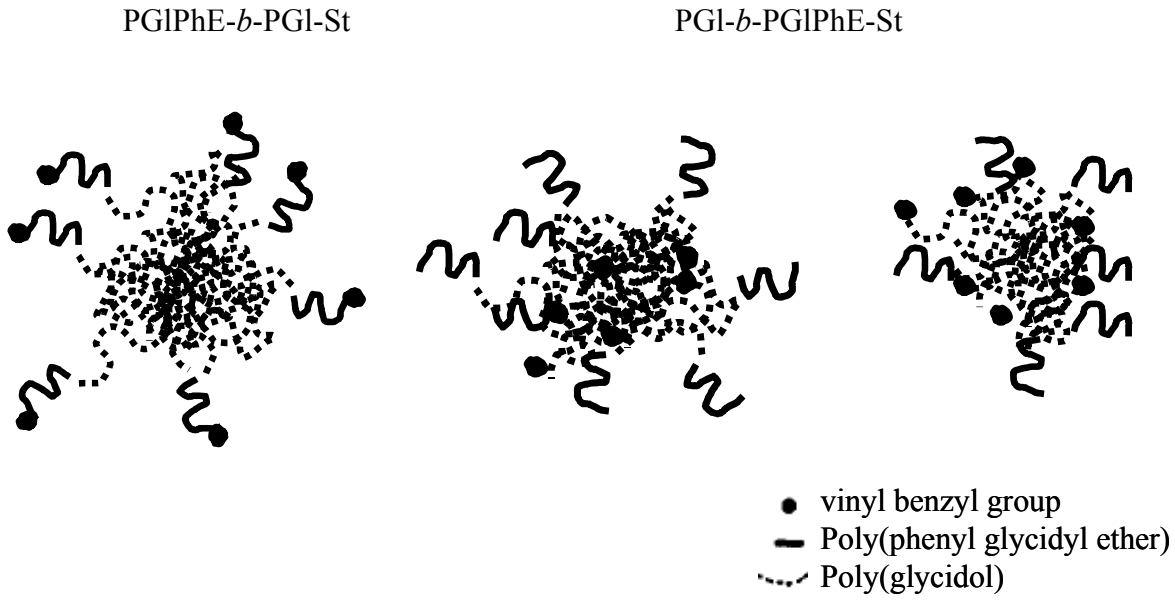


Figure 6.20. The structure of micelles formed by block macromonomers in THF.

Size of the micelles formed in THF was even smaller then in water, what was rather expected as the poly(phenyl glycidyl ether) block which is the only part of the block macromonomer soluble in THF was much shorter then insoluble poly(glycidol). So called *crew-cut micelles* were formed. Similarly as in water the size of the micelles was independent on the concentration of macromonomer in the investigated concentration range 0,5 to 10 g/L.

From the static light scattering measurements M_w and the aggregation numbers of the formed in THF micelles were found. The results are presented in Table 6.10.

Table 6.10. Parameters of macromonomers in THF according to *SLS*.

Sample	*dn/dc* in THF	M_n in DMF [g/mol]	M_w of micelle [g/mol]	*N*
PGl_{52}-*b*-$PGlPhE_8$-St	0,096	5900	480 000	80
$PGlPhE_9$-*b*-PGl_{54}-St	0,081	6000	578 000	96

As it can be seen the aggregation numbers are similar to the one measured for the micelles formed by the corresponding macromonomers in water.

Taking into account the results obtained from *DLS* and *SLS* measurements in water and in THF, it seems that the poly(glycidol) chains are in water in stretched conformation, as it is a good solvent of highly hydrophilic chains. The small, dense core of poly(phenyl glycidyl ether) is then surrounded by large corona, which size influences the R_h of the micelle considerably. From the other side in THF the situation is opposite. Although the similar amount of chains forms the micelle the relatively long poly(glycidol) chains insoluble in THF form the core surrounded by small shell of soluble poly(phenyl glycidyl ether). As the result formed micelles are smaller then in water.

6.1.7. *AFM* studies of micellization in water

AFM measurements of obtained micelles were also performed in order to get deeper insight into the morphology and structure of the micelles. Sample used for the measurements were prepared by dropping of the solution of macromonomers above their *CMC* value 0,9 g/L (PGl_{52}-*b*-$PGlPhE_8$-St) and 10 g/L (PGl_{55}-St) on the mica surface. The excess of the solution was removed by weak centrifugal forces and sample was left exposed to air and dried. The obtained *AFM* images are presented in Figure 6.21.

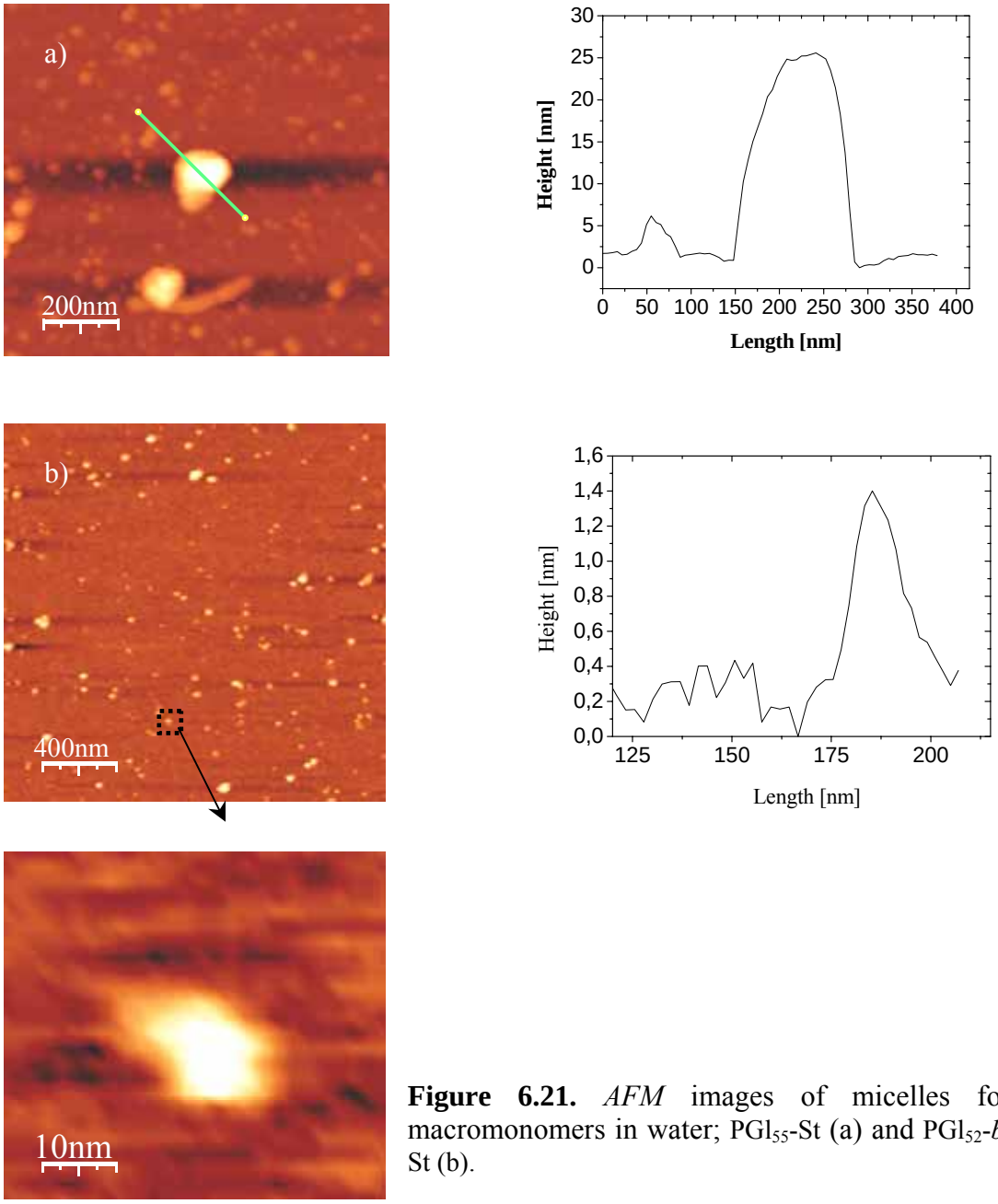


Figure 6.21. *AFM* images of micelles formed by macromonomers in water; PGl_{55}-St (a) and PGl_{52}-*b*-$PGlPhE_8$-St (b).

The micelles appeared on AFM images as smooth spheres, where the core-shell structure could not be resolved. The diameter of investigated micelles was found to be approximately 25 nm and 150 nm for PGl_{52}-*b*-$PGlPhE_8$-St and PGl_{55}-St, respectively. In both cases the sizes were about three times higher then obtained upon *DLS* measurements. However, the height of the particles was much smaller than their diameter what means that the micelles were strongly flattened upon drying increasing their size. Nevertheless, in both cases more or less spherical shapes of micelles and narrow size distribution was observed.

6.2. Polymerisation of macromonomers

As it was mentioned in the introduction part the polymerisation of macromonomers in organic solvents usually leads to low degrees of polymerisation, slow polymerisation rate and low degrees of conversion. The reason is the steric screening of the propagation center by the branched structure formed in the polymerisation, which hampers the access of the polymerizable group to the reaction centers. However, the high degrees of polymerisation were obtained upon polymerisation in water for amphiphilic macromonomers consisting of poly(ethylene oxide) chains terminated with reactive double bonds. Additionally, the polymerisation of such macromonomers was fast with almost quantitive conversion of macromonomers.

The different behaviour of PEO macromonomers during polymerisation in water was assigned to amphiphilic properties of this macromonomer and its ability to self-organization into micellar structure in selective solvent like water (for different parts of the molecule). In such solvent which is a good for one part and bad or non-solvent for the second part, micellar structures are formed. This aggregation locally concentrates and orients the hydrophobic polymerising groups, which enhances and accelerates their polymerisation[124-128].

In the previous chapter the *DLS* measurements confirmed that similar as in the case of amphiphilic PEO macromonomers [8] all synthesised poly(glycidol) macromonomers form micellar structures in water with hydrophobic cores and hydrophilic shells. Moreover, the organization of block macromonomers into micelles in THF was observed, where poly(glycidol) formed the core of the structure surrounded by soluble poly(phenyl glycidyl ether). Thus, taking into account that organization of macromonomers enhance the polymerisation water and THF were used as solvents for polymerisation of synthesised macromonomers.

6.2.1. Homopolymerisation of poly(glycidol)-based macromonomers

In the following chapter the conventional radical and controlled radical polymerisation (*ATRP*) of synthesised macromonomers will be described. Regardless of the type of applied polymerisation the only part of macromonomers which is involved in reaction is the reactive vinyl benzyl group. The homopolymerisation provides thus regular structures with poly(styrene) main chain and poly(glycidol) or poly(glycidol)-block-poly(phenyl glycidyl ether) side chains.

6.2.1.1. Detection of macromonomer conversion and molecular weight of polymacromonomers

As it was presented in the previous chapters all synthesised macromonomers are the mixture of functionalized macromonomer and non-functionalized oligomer inert upon polymerisation. The degree of functionalisation of all macromonomers varies, where the maximal value is about 69-74 %. However, it would be problematic to compare results such as conversion of macromonomers while each of the macromonomer has different functionality. It would not be clear if the macromonomer able to polymerise has already reach the full conversion or is still present in the reaction mixture. **However, as the maximal conversion of macromonomer is equal its degree of functionalisation for simplicity in all cases the conversion of macromonomers was divided by the functionalisation of macromonomer used for reaction.** For instance 69 % conversion of the used substrate with functionality 70% refers then to almost quantitive conversion of macromonomer. The residue is the non-functionalized oligomer unable to polymerisation.

The polymerisation of the macromonomers was monitored by both ^{1}H NMR spectroscopy and SEC chromatography. The ^{1}H NMR spectra were used in order to confirm that the polymerisation of macromonomer occurred. The behaviour of the peaks deriving from vinyl benzyl groups was observed. Upon polymerisation the intensity of the peaks and the value of integral was decreasing in comparison to that of *t*-butyl group of initiator and after the full conversion of the macromonomer no signals in the region 5 - 6 ppm was observed, whereas the intensity of the initiator group remained unchanged. The estimation of precise conversion of macromonomers was problematic using this method, as the intensity of the end group especially at high conversion of macromonomer was very low what increases the error of the calculations. Nevertheless, in some cases application of that method was inevitable as lack of separation of the polymerisation product from the unreacted residue was obtained upon *SEC-MALLS* measurements as presented in Figure 6.22.

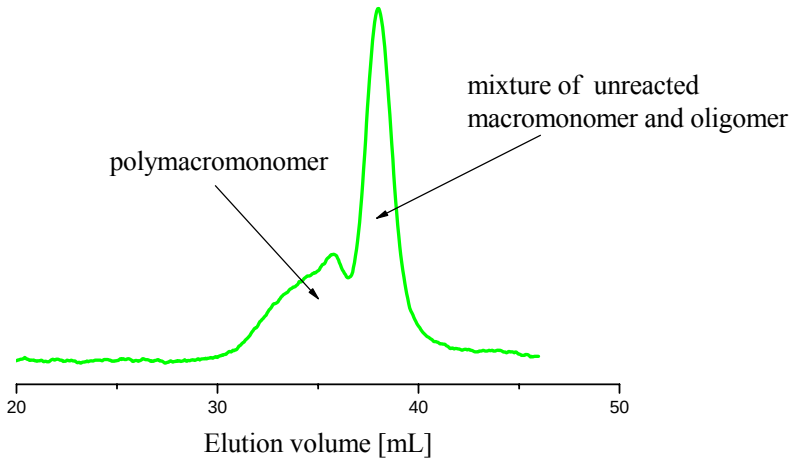


Figure 6.22. *SEC* trace of polymacromonomer weakly separated from unreacted residue.

In such cases the conversion of macromonomers was calculated according to the equation 6.2.

$$\%conversion_{macromonomer} = \frac{I_{vinylbenyzl}}{I_{initiator} \cdot DF} \cdot 100\% \qquad \textbf{(6.2.)}$$

$I_{vinylbenzyl}$ –intensity of one proton from vinyl benzyl group

$I_{initiator}$ –intensity of one proton from initiator *t*-butyl group

DF – degree of functionalisation of macromonomer

In case when polymerisation products and unreacted residues were well separated from each other as presented in Figure 6.23. *SEC* chromatograms were used to determine the conversion of macromonomers.

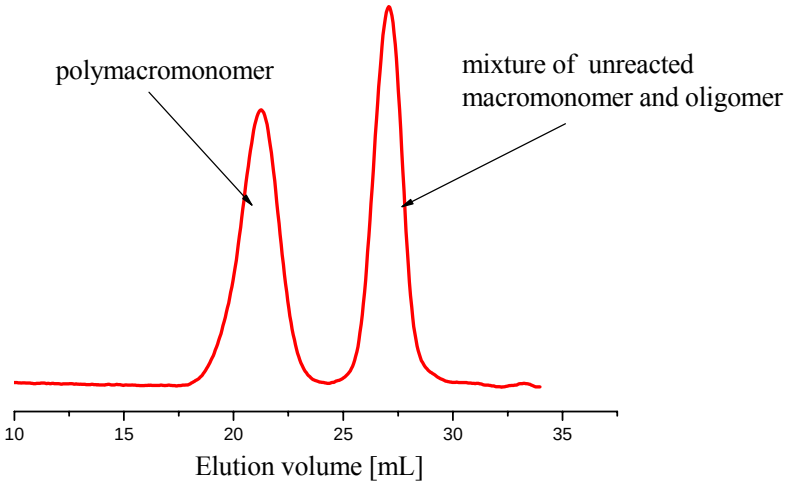


Figure 6.23. *SEC* trace of polymacromonomer well separated from unreacted residue.

Conversion of the macromonomers was calculated as the ratio of the surface under the polymacromonomer peak and the surface under unreacted residue peak (mixture of oligomer and macromonomer). The obtained conversion was normalized by the degree of functionalisation to give the real conversion of macromonomer able to polymerise.

$$\%conversion = \frac{S_{polymacromonomer}}{S_{unreacted}} \cdot 100\% \qquad \textbf{(6.3.)}$$

$S_{polymacromonomer}$ – the surface of the peak obtained for polymacromonomer

$S_{unreacted}$ – the surface of the mixture of unreacted macromonomer and oligomer unable to polymerise

The calculation of molecular weights of the polymacromonomers from ^{1}H NMR was impossible. Thus, M_n were determined according to *SEC-MALLS* measurements using refractive index increments determined for macromonomers. Generally, the determination of the molecular weights of branched macromolecules is a challenging task. The difficulties are due to the imperfections of the chromatographic separation and difficulties in the absolute molecular weight detection. Even chemically homogenous branched polymers are frequently not properly separated in the *SEC* columns. In addition, in the case of amphiphilic macromolecules, which contain the segments of very different philicity as the amphiphilic polymacromonomers, the distribution of the chemical composition changes the overall interactions with the solvent, thus disturbing the relationship between the hydrodynamic volume and the molecular weight. Even if the chromatographic separation is proper, the detection of the molecular weight in the eluent slices causes problems.

The necessary, however not always sufficient condition for the correct molecular weight determination by *SEC*, the linearity of the molecular weight versus elution volume plot is well fulfilled for all obtained polymacromonomers. The example is presented in Figure 6.24. That confirms that regardless on the structure good separation of the branched polymers according to the molecular weight was achieved on the applied columns set. The measured values of the M_n of polymacromonomers are thus correct.

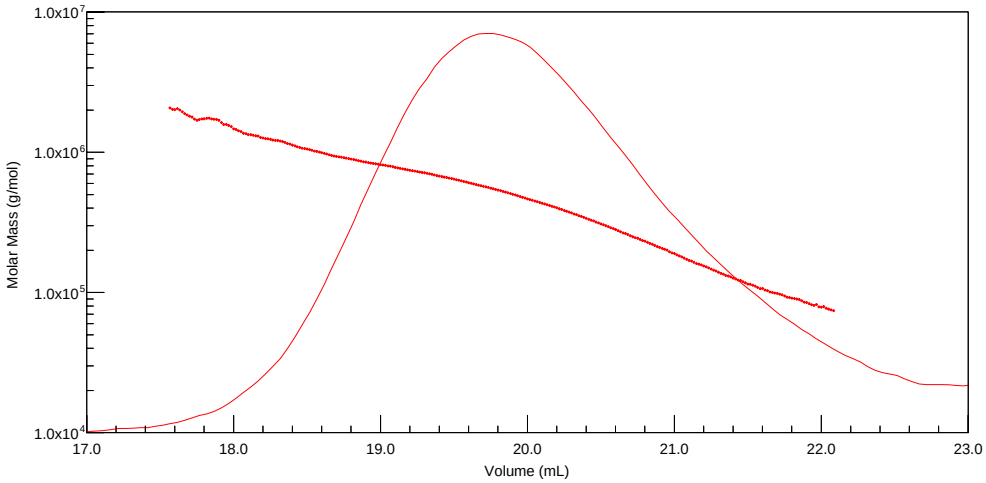


Figure 6.24. The example trace of molecular weight vs. elution time for polymacromonomer.

6.2.2. Free radial polymerisation of macromonomers in water

The conventional radical polymerisation of the amphiphilic poly(glycidol) macromonomers was carried out in two different polymerisation systems:

- in water using *AVA* (*4,4'*-azobis (*4*-cyanovaleric acid)) as initiator (T = 60 °C);
- in water/benzene mixture of the volume ratio 10:1 v/v using *AIBN* (*2,2'*-azobis(isobutyronitrile) as initiator, T = 70 °C.

The first conditions of polymerisation are the same as applied by Ito et al. upon micellar polymerisation of amphiphilic ethylene oxide macromonomers [21-24].

The second system was invented in order to enhance the reaction between initiator and reactive hydrophobic group of the macromonomer using the hydrophobic compound (*AIBN)*. The hydrophobic initiator was expected to penetrate into the hydrophobic core of the structure and to initiate the polymerisation of macromonomers in the region where the concentration of reactive groups is the highest. Since the applied initiator is water insoluble, it was introduced as benzene solution into the water reaction medium, preserving the same water to benzene volume ratio of 10/1 in all experiments. The hydrophobic solvent was also expected to penetrate the hydrophobic part of the aggregates were the polymerizable groups are concentrated, thus further increasing the polymerisation.

6.2.2.1. Rate of polymerisation of macromonomers

The kinetics of polymerisation of poly(glycidol)-type macromonomers are presented in Figure 6.25 and 6.26.

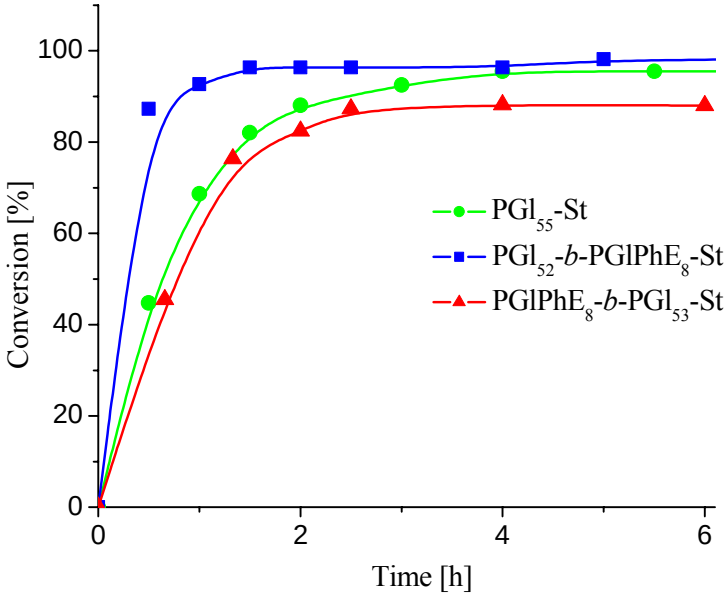


Figure 6.25. Polymerisation of macromonomers in water using *AVA*, $C_{macromonomer}$ = 0,20 g/mL, T = 70 °C.

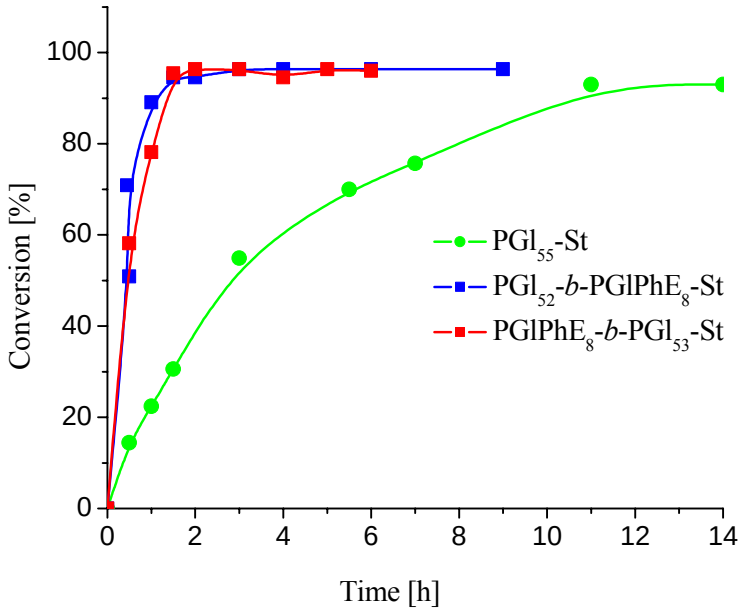


Figure 6.26. Polymerisation of macromonomers in water/benzene mixture 10/1 v/v using *AIBN*, $C_{macromonomer}$ = 0,20 g/mL, T = 70 °C.

As it an be seen the conversion of macromonomers was regardless of the polymerisation system as well as of the type of macromonomer. In all cases after the certain period of time the conversion reached the level of 90 % or more and remained unchanged upon further heating. Also the introduction of fresh portion of initiator did not influence the conversion.

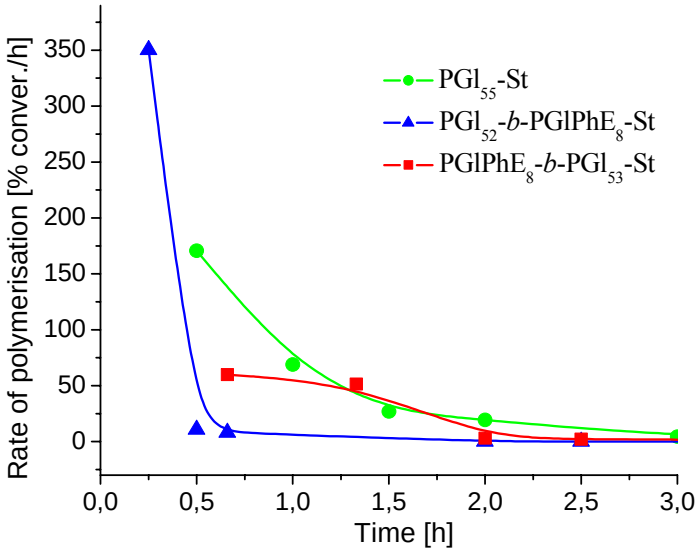


Figure 6.27. The dependence of rate of polymerisation versus time upon polymerisation in water; $C_{macromonomer}$ = 0,20 g/mL, T = 70 °C.

Similarly as in case of PEO macromonomers the polymerisation of macromonomers in water initiated with *AVA* was fast as after about 2 hours the conversion of all investigated macromonomers reached the constant value. The rate of polymerisation in water was extremely high in case of PGl_{52}-*b*-$PGlPhE_8$-St, while the lowest value was observed for $PGlPhE_8$-*b*-PGl_{53}-St.

Such behaviour seems to be the consequence of the structure of micelles formed by macromonomers in water. The compartmentalization of the reaction loci decreases the termination rate [21-24]. As a consequence the rate of polymerisation (propagation step) increases. PGl-*b*-PGlPhE-St forms the most compact well-organized micelles with the unsaturated groups gathered in the core as was presented in the Figure 6.18. In case of PGl-St the formed micelles are larger and less compact, what leads to the decrease of R_p of half in comparison to PGl-*b*-PGlPhE-St. The lowest rate of polymerisation obtained for PGlPhE-*b*-PGl-St may result from two facts: firstly the polymerisation product precipitates from water upon reaction, what causes the interruption of the polymerisation chain; secondly although it forms compact micelles the reactive groups probably do not take part in the formation of the

hydrophobic core and are concentrated at the shell. As the result the local concentration of the reactive groups is lower then in case of the other macromonomers.

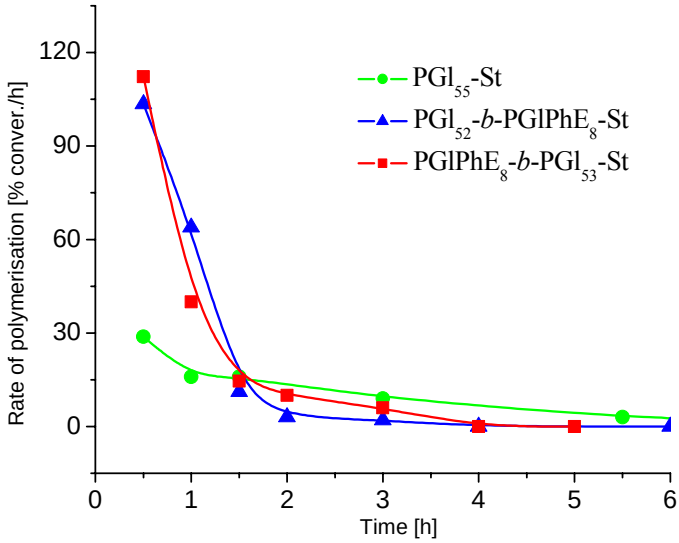


Figure 6.28. The dependence of rate of polymerisation versus time upon polymerisation in water/benzene mixture 10/1 v/v; $C_{macromonomer}$ = 0,20 g/mL, T = 70 °C.

Upon the polymerisation of macromonomers in the mixture of water/benzene for PGl_{55}-St and PGl_{52}-*b*-$PGlPhE_8$-St the rate of polymerisation decreased about four-times in comparison to the polymerisation carried out in pure water. For PGl_{55}-St 11 hours was needed to reach 93 % of conversion, where in pure water the same value was reached after 2 hours.

Such behaviour seems to be the effect of two opposite phenomena. From one side the hydrophobic initiator penetrating the hydrophobic core of the structure initiated the polymerisation of macromonomers in the region where the concentration of reactive groups was the highest. However, as it was introduced as the benzene solution the swollen micelles were formed. The local concentration of the double bonds in the micelle core decreased leading to the decrease of the reaction rate. Since the decomposition rate of *AVA* in water and *AIBN* in benzene were found to be only a little different from each other, it can not be the reason of the lower rate of polymerisation.

Nevertheless, the different behaviour was noticed for $PGlPhE_8$-*b*-PGl_{53}-St. In the water/benzene mixture the R_P of polymerisation increased of 100 % in comparison to polymerisation in pure water and was on the level of the value obtained for PGl-*b*-PGlPhE-St macromonomer. Under such condition the full conversion of the macromonomer was reached after 1 hour. Additionally, slightly higher conversion (~ 5%) of macromonomer was observed.

In case of PGlPhE$_9$-*b*-PGl$_{53}$-St the formation of swollen micelles enhanced thus the polymerisation rate. It can be the effect of the increase of the local concentration of vinyl benzyl reactive groups in the core of the micelle as the effect of formation of the loop by poly(glycidol) chains. As the result the hydrophobic polymerizable groups were involved in formation of the core of the swollen micelle. The other possibility is the increase of the solubility of the growing radical upon polymerisation. As it was stated the polymacromonomer obtained upon polymerisation of PGlPhE$_9$-*b*-PGl$_{53}$-St is insoluble in water, but soluble in benzene. It is thus possible that especially at the beginning of the reaction the presence of the cosolvent improved the solubility of the growing radical, what resulted in the increase of the polymerisation rate.

6.2.2.2. Influence of conversion on the M_w of polymacromonomers

The typical behaviour observed usually upon radical polymerisations was noticed upon polymerisation of macromonomers as well. Regardless of the polymerisation system or macromonomer type the molecular weight of polymacromonomers was decreasing with increase of the conversion of macromonomer as can be seen in Figure 6.29.

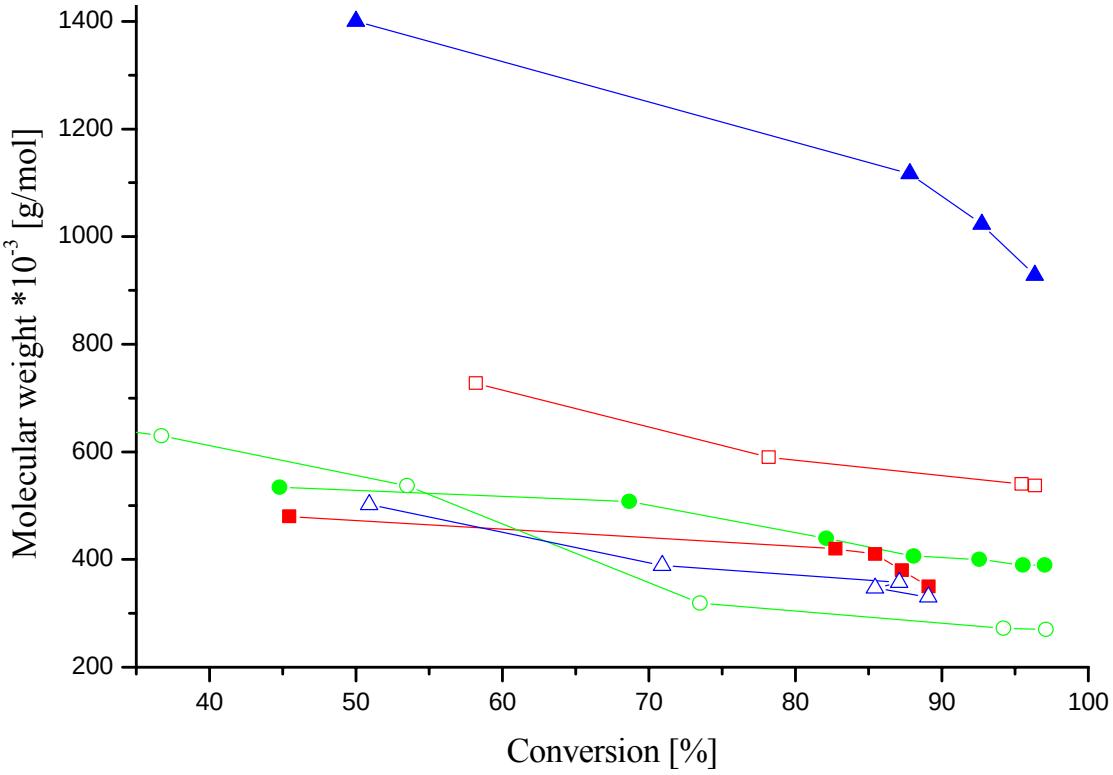


Figure 6.29. Change of molecular weight of polymacromonomers versus conversion. O – PGl$_{55}$-St, Δ – PGl$_{52}$-*b*-PGlPhE$_8$-St, □ - PGlPhE$_8$-*b*-PGl$_{53}$-St; closed symbols - polymerisation in water, open symbols polymerisation in water/benzene mixture; c = 0,20 g/mL.

The decrease of the molecular weight of polymacromonomer was accompanied by increase of the polydispersity of the product (Figure 6.30). The largest change of M_w/M_n indices were observed at the end of polymerisation, when the conversion of macromonomers exceeded 85 %. However, at the end of the reaction (low concentration of macromonomers) the termination by recombination of two growing radicals become less privileged. From the other side interruption of the growing chains by presence of impurities, which influence at this step of polymerisation becomes larger, is more pronounced. Thus, in the system appears the fraction of the products with low molecular weight what significantly influences the polydispersity of the product.

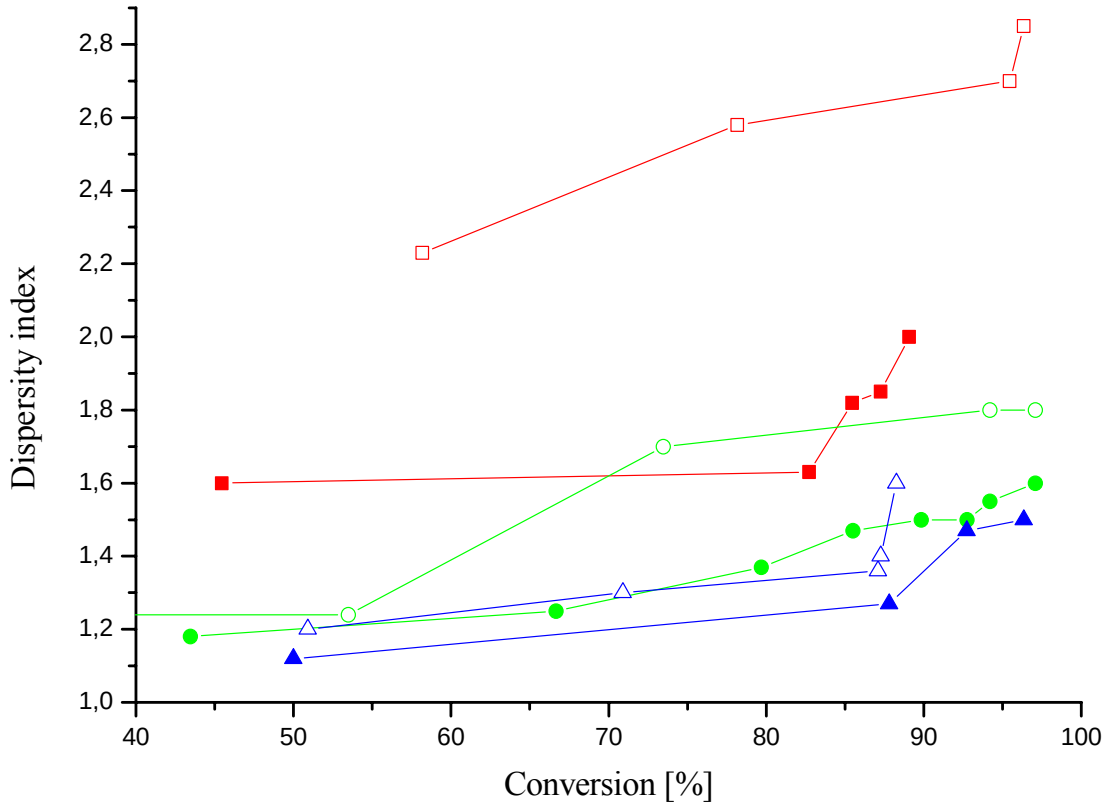


Figure 6.30. Influence of conversion on the polydispersity of polymacromonomers. O – PGl_{55}-St, Δ – PGl_{52}-*b*-$PGlPhE_8$-St, □ - $PGlPhE_8$-*b*-PGl_{53}-St; closed symbols - polymerisation in water, open symbols polymerisation in water/benzene mixture; $C_{macromonomer}$ = 0,20 g/mL.

The example *SEC* traces of the change of molecular weight of polymacromonomer with increase of the conversion is presented in Figure 6.31. As it can be seen the peak deriving from polymacromonomer becomes broader with increase of the conversion mostly because of appearance of low molecular weight fraction in the elution volume range 25-29 mL. **It should be added that as it is not easy to present the parallel increase of the polymacromonomer peak and decrease of the reacting macromonomer the curves were normalized so that the amount**

of the unreacted residue was equal in each case. This solution led to easy monitor the creation of polymacromonomer with increase of conversion and will be also used in the further part of that work.

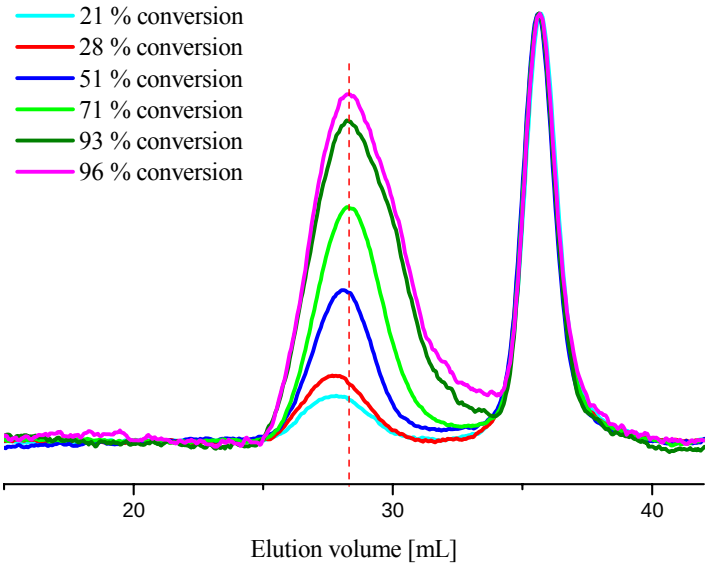


Figure 6.31. SEC traces of polymerisation product at different conversion of macromonomer PGl_{55}-St, polymerisation in water, $C_{macromonomer}$ = 0,2 g/mL, T = 60 °C.

6.2.2.3. Influence of macromonomer concentration on the molecular weights and polydispersities of polymacromonomers

The influence of concentration on the degree of polymerisation of polymacromonomers and on M_w/M_n indices is presented in Figure 6.32 and 6.33.

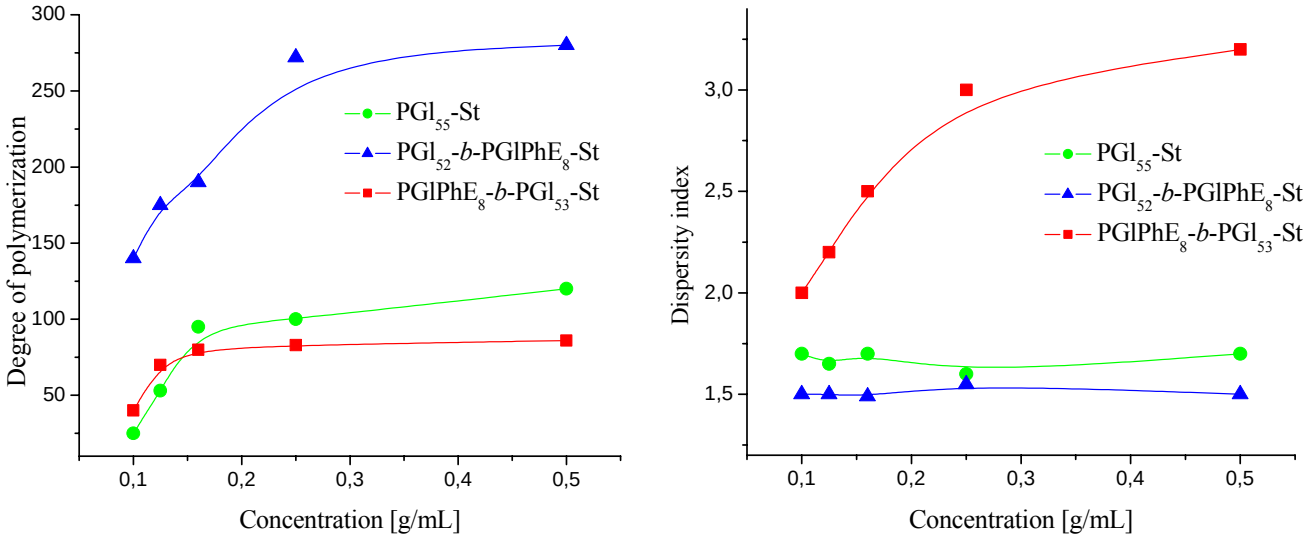


Figure 6.32. Influence of macromonomer concentration on *DP* of polymacromonomer upon polymerisation in water; $C_{macromonomer}$ = 0,2 g/mL, T = 60 °C.

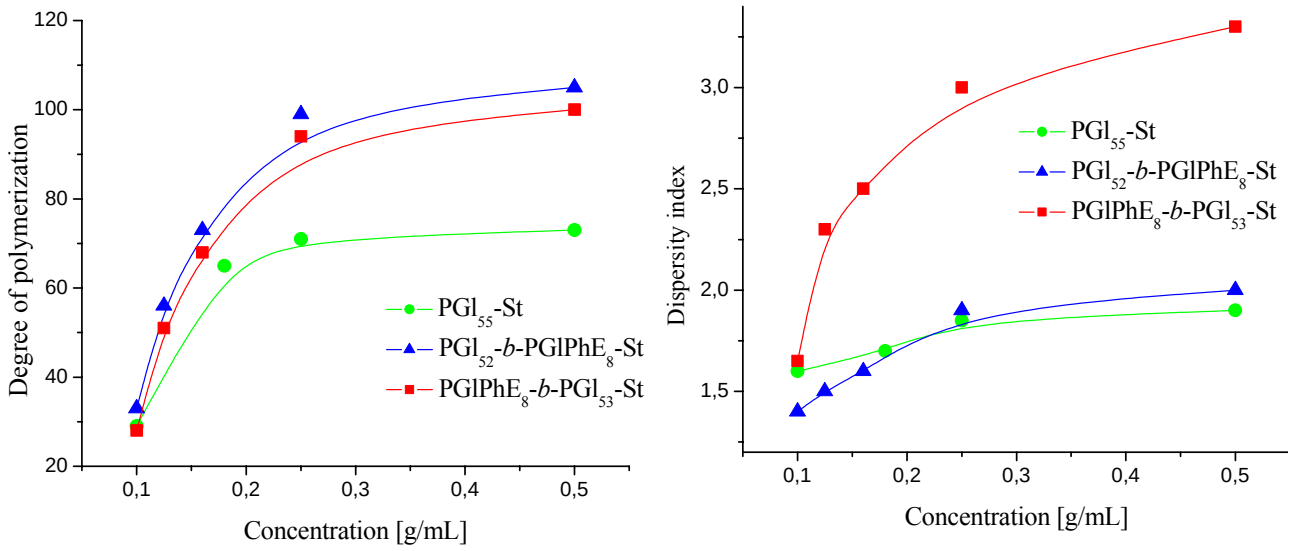


Figure 6.33. Influence of macromonomer concentration on *DP* of polymacromonomer upon polymerisation in water/benzene mixture 10/1 v/v.

The conversion of macromonomers was only slightly dependent on its concentration in the reaction mixture and in most cases reached about 90%.

As in the case of the PEO macromonomers [22], the degree of polymerisation of polymacromonomers was increasing with increased initial concentration of the macromonomers in the reaction mixture regardless of the polymerisation system or macromonomer type. However, in all cases above a certain concentration (about 0,2 g/mL) *DP* of the products varied only moderately by the effect of concentration of macromonomer.

The increase of the molecular weight of the polymacromonomers obtained in the mixture water/benzene was accompanied with an increase of the dispersity of the product. This may suggest that polymerisation took place in non-uniform benzene swollen micellar aggregates of different sizes. On the other side upon polymerisation in water polydispersity of the polymacromonomers was independent on the macromonomer concentration, with exclusion of the polymacromonomers of PGlPhE$_8$-*b*-PGl$_{53}$-St, suggesting formation of uniform micelles.

In the case of PGl$_{52}$-*b*-PGlPhE$_8$-St and PGl$_{55}$-St the molecular weights of polymacromonomers obtained upon polymerisation in water were higher than that obtained upon polymerisation in the benzene/water mixture at the same concentration. The opposite effect was observed for PGlPhE$_8$-*b*-PGl$_{53}$-St where introduction of benzene to the

polymerisation system slightly increased the *DP* of the polymacromonomer. However, as was mentioned polymacromonomer obtained from PGlPhE$_8$-*b*-PGl$_{53}$-St is insoluble in water and precipitates from the reaction mixture upon reaction. It leads to the interruption of the growing polymer chain and as the result the molecular weights of products decreases while the M_w/M_n increases. The introduction of benzene which is the solvent of that polymacromonomer enhance the solubility of the growing radical and higher molecular weights of polymacromonomers can be obtained. Nevertheless, the M_w/M_n still remained high.

The maximal *DP* of polymacromonomers obtained from PGlPhE$_9$-*b*-PGl$_{53}$-St was similar to the aggregation number found for the corresponding macromonomer used for polymerisation. In the case of the polymacromonomers obtained upon polymerisation of PGl$_{52}$-*b*-PGlPhE$_8$-St the degree of polymerisation of the products were about two times higher than the aggregation numbers in the micelle of the corresponding macromonomer found during *SLS* measurements. This result may suggest that the micellar polymerisation involved the intermicellar propagation or termination or reorganization of the micelle during polymerisation. Nevertheless, it should be remembered that the light scattering measurements were made at 25 °C at concentrations much more diluted as compared to those in polymerisation. It was found that the micelle formation is more favoured with increasing temperature and at higher temperature and concentration the micelles of larger size may grow [243]. Thus, it can not be excluded that the polymerisation of this macromonomer proceeded mainly within micelles with some additional macromonomers from the surrounding area. This seems to be correct as M_w/M_n and the *DP* of the product at high concentration only slightly depends on the concentration of macromonomer in polymerisation mixture.

In the region of lower concentrations *DP* of polymacromonomers were much lower than the aggregation numbers found for this macromonomers upon *SLS* measurements. This may indicate that at this concentration range the termination by recombination of the growing radicals is less privileged.

6.2.3. Controlled polymerisation of macromonomers in water

The controlled polymerisation of poly(glycidol) macromonomers in water was initiated with a well-defined PEO_{2000}-Br macroinitiator (α-methoxy-ω-bromopropionate poly(ethylene oxide)) in the presence of catalyst *Cu^{I}-Me_6TREN*. The reaction was carried out at room temperature. The behaviour of PGl_{52}-*b*-$PGlPhE_8$-St upon polymerisation was different from the one observed in case of $PGlPhE_8$-*b*-PGl_{53}-St or PGl_{55}-St so will be described separately.

6.2.3.1. *ATRP* polymerisation of PGl-*b*-PGlPhE-St

- ***Kinetic measurements***

To demonstrate the character of polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St kinetics experiments were performed. Samples were drawn at given reactions times and analysed by *SEC-MALLS* chromatography. The results are presented in Figure 6.34.

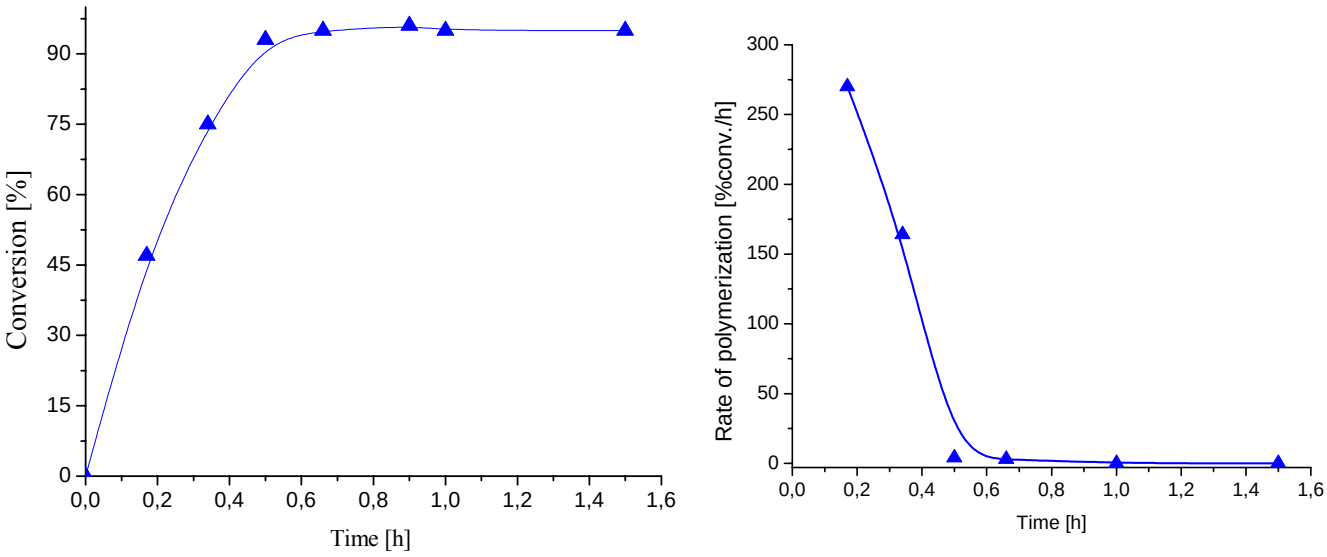


Figure 6.34. The conversion vs. time and rate of polymerisation vs. time upon *ATRP* of PGl_{52}-*b*-$PGlPhE_8$-St; molar ratio [PGl-*b*-PGlPhE-St]/[PEO-Br]/[CuBr]/[Me_6TREN] = 50/1/2/2, $C_{macromonomer}$ = 0,20 g/mL, RT.

The *SEC* analysis of reaction mixture showed formation of monomodal polymacromonomer of the polydispersity index 1,15 confirming successful initiation of polymerisation of the macromonomer by PEO macroinitiator. As it can be seen in Figure 6.34. the *ATRP* of PGl_{52}-*b*-$PGlPhE_8$-St macromonomer smoothly occurred without an induction period. Although the polymerisation was carried out at room temperature the reaction time was shorter in

comparison to the conventional radical polymerisation of that macromonomer in water or in the mixture of water/benzene. Almost complete conversion of functionalized macromonomer was obtained very fast in the less then 40 min. It confirms that the suppression of termination increase the reaction rate.

The Figure 6.35. shows the $-ln(M/M_0)$ versus time and molecular weight versus conversion curves. As it can be seen the obtained results confirmed the controlled character of polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St in the presence of Cu^I-*Me*$_6$*TREN* catalyst. The obtained linear plot of $-ln(M_0/M)$ versus time indicates the constant concentration of active radicals upon the reaction (suppressed termination). The molecular weight of polymacromonomer was increasing with the conversion where deviation from the linear trend were not observed even at the end of the reaction.

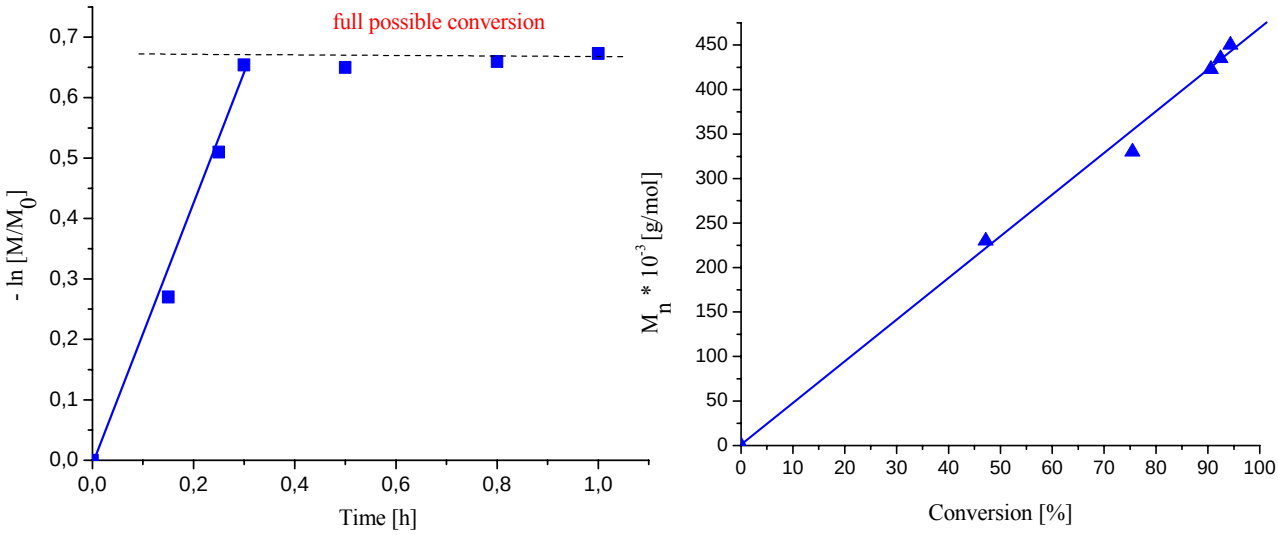


Figure 6.35. The dependence of $ln(M_0/M)$ vs. time and molecular weight vs. conversion upon *ATRP* of PGl_{52}-*b*-$PGlPhE_8$-St; molar ratio [PGl_{52}-*b*-$PGlPhE_8$-St]/[PEO-Br]/[CuBr]/[*Me*$_6$*TREN*] = 50/1/2/2, $C_{macromonomer}$ = 0,20 g/mL, RT.

The increase of the molecular weight of polymacromonomer was accompanied by decrease of the elution volume as shown on the SEC traces of samples drawn at different conversion of macromonomer in Figure 6.36. Moreover, at the end of polymerisation where the full conversion of functionalized macromonomer was obtained the degree of polymerisation of polymacromonomer was very close to targeted (taking into account the functionalisation of used macromonomer).

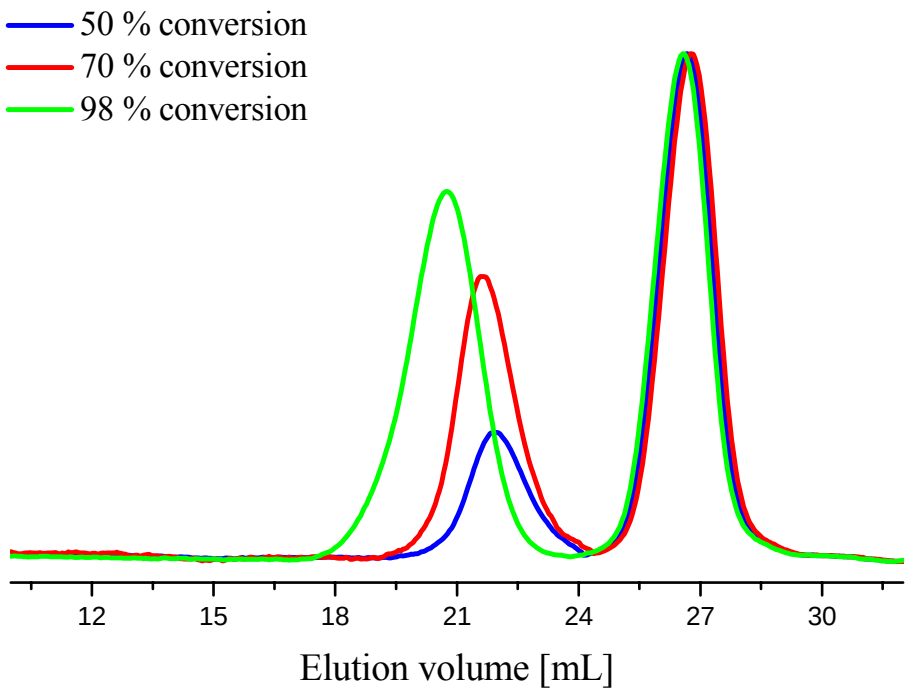


Figure 6.36. SEC traces of polymacromonomers at different conversion of macromonomer upon polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St, $C_{macromonomer}$ = 0,20 g/mL, RT.

- ***Estimation of DP***

Upon controlled polymerisation the number of active sites in a batch is constant and equal to the number of initiator molecules introduced at the onset of reaction. As the consequence, the number-average degree of polymerisation can be determined by the molar ratio of monomer converted to initiator that is used. The *DP* of the product can be then influenced once the molar distribution within a prepared sample is expected to be rather narrow.

The influence of the [PGl_{52}-*b*-$PGlPhE_8$-St]/[PEO-Br] molar ratio on the molecular weight and M_w/M_n indices of the polymacromonomers is presented in Figure 6.37.

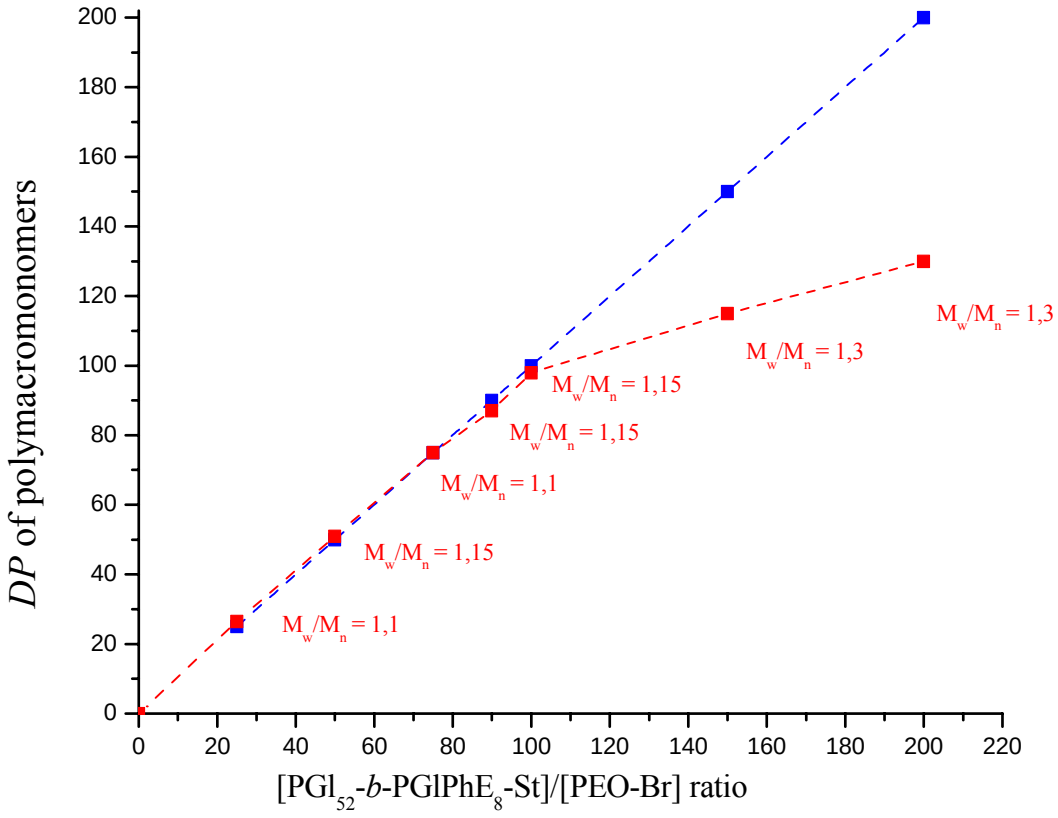


Figure 6.37. The influence of [PGl_{52}-*b*-$PGlPhE_8$-St]/[PEO-Br] ratio on the molecular weight and M_w/M_n of the polymacromonomer; blue symbols - targeted values, red symbols – obtained values .

As it can be seen up to ratio of [PGl-*b*-PGlPhE-St]/[PEO-Br] = 100 the obtained *DP* of polymacromonomer was equal to the targeted value. The polydispersity of the products was very low not exceeding 1,15. However, above this value deviations from the linear line were observed. The molecular weights of the products were much lower then targeted once while their polydispersities increased.

Taking into account controlled character of the reaction this was rather unexpected. However, that seems to confirm that the polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St proceeds in the core of the formed micelles with some additional non organised macromonomers. The intermicellar propagation did not occur. The maximal value of the polymacromonomer molecular weight is then limited, however, using controlled polymerisation can influenced in some range.

6.2.3.2. Controlled polymerisation of PGlPhE$_8$-*b*-PGl$_{53}$-St and PGl$_{55}$-St macromonomers in water

The results obtained upon *ATRP* of PGl$_{55}$-St and PGlPhE$_8$-*b*-PGl$_{53}$-St were different then that obtained upon polymerisation of PGl$_{52}$-*b*-PGlPhE$_8$-St. The first macromonomer did not polymerised under applied conditions at all while PGlPhE$_8$-*b*-PGl$_{53}$-St showed only very low conversion, lower then 10 %. The repeated introduction of catalyst and initiator did not improved the results for PGl$_{55}$-St, while a slight increase of conversion was observed for PGlPhE$_8$-*b*-PGl$_{53}$-St. However, as it can be seen in Figure 6.38 the obtained product was bimodal.

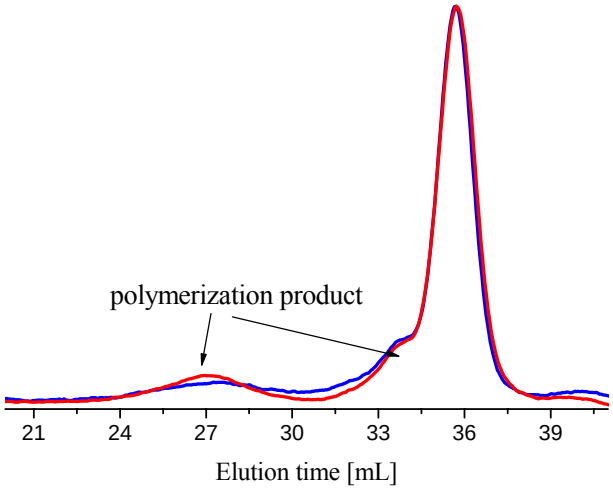


Figure 6.38. *SEC* traces obtained upon *ATRP* of PGlPhE$_8$-*b*-PGl$_{53}$-St in water; molar ratio [PGlPhE$_8$-*b*-PGl$_{53}$-St]/[PEO-Br]/[CuBr]/[*Me$_6$TREN*] = 50/1/2/2, $C_{macromonomer}$ = 0,20 g/mL, RT.

Generally, upon *ATRP* at initiation step, initiator (for instance PEO–Br) reacts with the catalyst system and through abstraction of halogen from the appropriate organic halide radical of PEO$^{\bullet}$ and oxidized metal catalyst system *Cu^{I}-Me$_6$TREN* occurs. The formed radical adds in the following step to the monomer to generate the propagation of the polymer chain. The rate of initiation of the polymerisation is fast or at least comparable to the rate of propagation. Under such conditions all initiator molecules initiate simultaneously polymerisation and remain attached to the growing chain. Thus, all chains start growing at the same time and as the termination is suppressed the growth is continued until all available monomer reacted. However, upon polymerisation of PGlPhE$_8$-*b*-PGl$_{52}$-St the growth of the chain was stopped when the polymerisation product became too hydrophobic and precipitated from water. As the

result all the moieties of macroinitiator became insoluble and the further growth of the polymerising chain was impossible.

The repeating addition of initiator after 6 h of polymerisation led to the initiation of the reaction and slight increase of conversion. It confirms that introduced catalysed was still active and if the growing polymacromonomer would remain soluble in water the further growth would probably appear.

The complete lack of conversion obtained for PGl_{55}-St was unexpected because as it was shown this macromonomer polymerised to high conversions upon radical polymerisation. However, in contrast to radical polymerisation *ATRP* is very sensitive on the presence of impurities especially of acidic character. Their presence in the system cause the deactivation of catalyst and the growth of the polymer chain is stopped. It is possible that the purity of the macromonomer PGl_{55}-St not enough so that it could be polymerised in *ATRP* system. In contrast to block macromonomers the removal of salts from PGl_{55}-St was done by ion exchangers not by dialysis, which usually gives the purest products. It is possible that some acidic groups from cation exchanger were introduced during that operation.

However, it can not be excluded that the impurities were introduced before for example with the solvents used for removal of excess of unreacted terminating agent (vinyl benzyl chloride). The precipitation of macromonomer or addition of active carbon did not improve the results as well and *ATRP* of PGl_{55}-St was unsuccessful under applied conditions.

6.2.4. Conventional radical polymerisation of block macromonomers in THF

The polymerisation of PEO macromonomers in THF using *AIBN* was reported [133], however the polymerisation in that solvent was hampered as these macromonomers does not aggregate in THF.

In case of poly(glycidol) block macromonomers the *DLS* measurements showed formation of well-defined micelles in THF what gave rise to investigation of the polymerisation behaviour of these macromonomers in THF.

6.2.4.1. Rate of polymerisation

The kinetic measurements of macromonomers polymerisation in THF were performed in order to demonstrate the character of polymerisation. The results are presented in Figure 6.39.

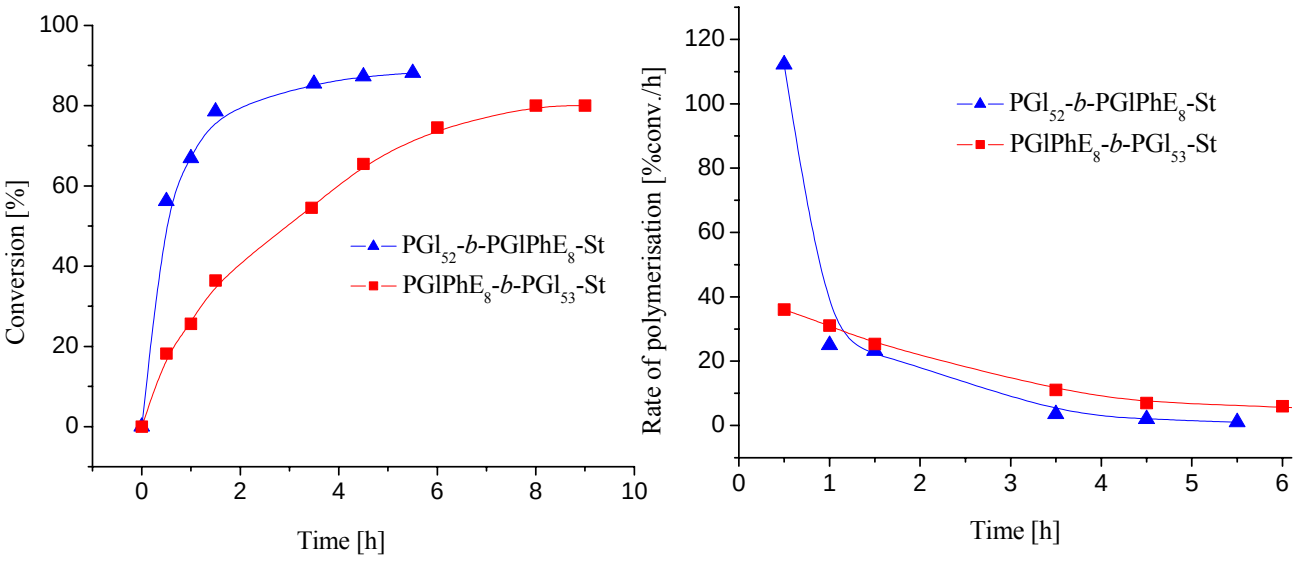


Figure 6.39. The conversion vs. time and rate of polymerisation vs. time upon polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St and $PGlPhE_8$-*b*-PGl_{53}-St in THF, $C_{macromonomer}$ = 0,10 g/mL, T = 60 °C.

The rate of polymerisation carried out in THF was about 3 times higher for $PGlPhE_8$-*b*-PGl_{53}-St in comparison to PGl_{52}-*b*-$PGlPhE_8$-St. Over 90 % of conversion of macromonomer PGlPhE-*b*-PGl-St was reached after 2 hours, while for the second type of macromonomer the unchanged value of conversion about 80 % was obtained after 8 hours.

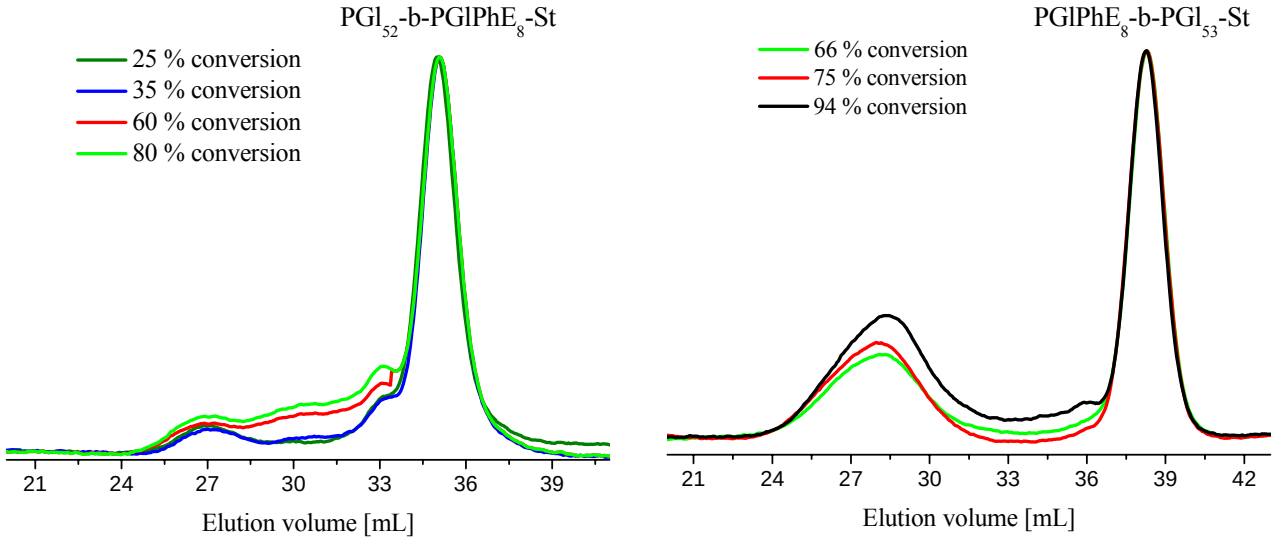


Figure 6.40. *SEC* traces of polymerisation products obtained at different conversions of macromonomer upon polymerisation of block macromonomers $PGlPhE_8$-*b*-PGl_{53}-St and PGl_{52}-*b*-$PGlPhE_8$-St in THF, $C_{macromonomer}$ = 0,10 g/mL, initiator *AIBN,* T = 60 °C.

In the Figure 6.40 are shown *SEC* traces of polymerisation products obtained at different conversion of macromonomers (conversion was normalized in the way described in section 6.2.2.2.). As it can be seen the product of polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St is multimodal with a high content of low molecular weight of oligomer and is badly separated from unreacted residue. In contrast $PGlPhE_8$-*b*-PGl_{53}-St gave products of high molecular weight, although at the end of polymerisation the formation of low molecular weight oligomer fraction was also observed.

The polymerisation behaviour of studied macromonomers in THF is in contrast to the results obtained upon polymerisation of these macromonomers in water where PGl_{52}-*b*-$PGlPhE_8$-St polymerised more rapidly and to much higher molecular weights then $PGlPhE_8$-*b*-PGl_{53}-St. However, as it was presented in Figure 6.20. in THF the micelles of the opposite structure then in water are expected. The core is formed by poly(glycidol) chains while short nevertheless soluble poly(phenyl glycidyl ether) chains constitute the shell.

In case of aggregates formed by PGl_{52}-*b*-$PGlPhE_8$-St the double bounds are concentrated at the shell of the micelle as was presented in Figure 6.20. The polymerisation behaviour of the opposite micelles formed by PEO macromonomers in hexane was observed Ito *et al*. The authors concluded that when the polymer chains are longer the "mobility" of reactive groups is higher and the polymerizable group can easier get together. As the result macromonomers with longer ($DP \approx 30$ - 43) chains polymerised faster and to higher degree of polymerisation. In the case of shorter chains ($DP \approx 15$ –20), what was also observed upon polymerisation of PGl-*b*-PGlPhE-St only low *DP*s were observed.

Another factor which influenced the polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St was the insolubility of obtained polymacromonomer in THF. It was precipitating from the reaction mixture upon polymerisation, what caused the decrease of the rate of polymerisation and molecular weight of macromonomers. As the formed polymacromonomer is highly hydrophilic it precipitates from THF fast what results in the polymacromonomers of *DP* not higher then 10. Nevertheless, similarly as it was observed by Ito *et al.* in hexane the increase of local concentration of reactive groups resulted in relatively high conversion of macromonomer above 80 %.

The structure of the aggregates formed by $PGlPhE_8$-*b*-PGl_{55}-St is a little different as the reactive vinyl benzyl groups are gathered in the core of formed aggregates or if poly(glycidol)

chains form loops at the border of the core and shell as was presented in Figure 6.20. However, as the rate of polymerisation is very high in this system the local concentration (distance between double bonds) of reactive groups is probably high, what allows to find the structure with poly(glycidol) loops as more probable. Additionally, no precipitation of obtained polymacromonomer from THF occurs.

6.2.4.2. Influence of macromonomer concentration on the molecular weights and polydispersities of polymacromonomers upon polymerisation in THF

In the figure 6.41. is presented the influence of macromonomer concentration on the molecular weight of polymacromonomer.

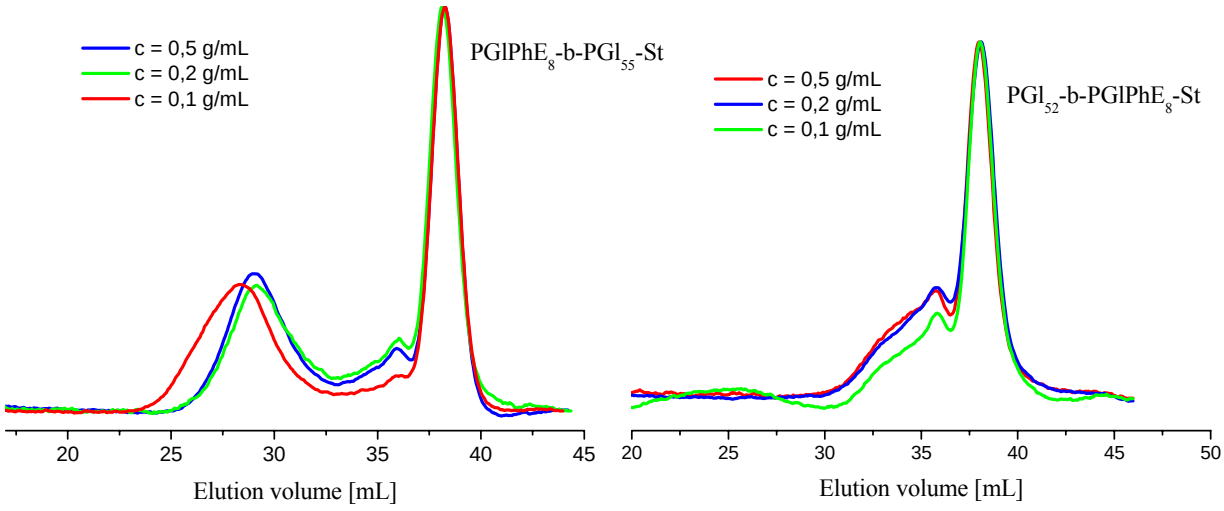


Figure 6.41. *SEC* traces of polymerisation products obtained upon polymerisation at different concentrations of block macromonomers, initiator *AIBN*, T = 60 °C.

As it can be seen regardless of the concentration of PGl_{52}-*b*-$PGlPhE_8$-St upon polymerisation the obtained polymacromonomer was badly separated from the mixture of unreacted macromonomer and not functionalized oligomer. In the studied concentration range the *DP* of multimodal polymerisation product was always lower then 10 oligomers.

The polymerisation of $PGlPhE_8$-*b*-PGl_{53}-St resulted in bimodal products with considerably different molecular weights, which were well separated from each other. The first peak was assigned to polymacromonomer of relatively high *DP*, where the value depended on the concentration of macromonomer during reaction. The second peak was assigned to the oligomer of very low molecular weight lower than 15000 g/mol (*DP* 3-4). However, as the

concentration of macromonomers in reaction mixture was decreased from 0,5 to 0,1 g/mL the amount of the oligomer in the polymerisation product was also decreased, while the molecular weight of polymacromonomer increased.

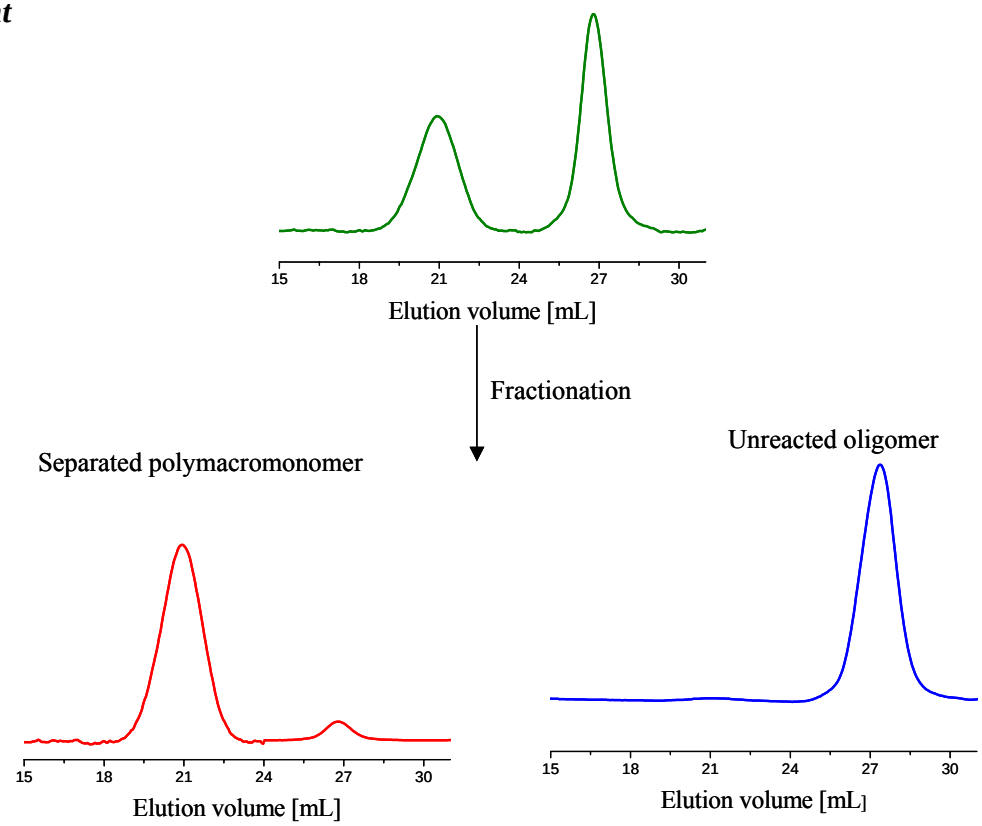
The bimodality of the product may suggest that two mechanisms of macromonomer polymerisation are parallel present in the system. As was shown in Figure 6.20. the block macromonomers forms micelles in THF where the reactive vinyl benzyl groups can be concentrated at the border of core and shell of the micelle or in the core formed by insoluble poly(glycidol). Thus, if the reactive groups are concentrated at the border of core and shell their local concentration is relatively high. As the result the polymerisation of this reactive groups occurs fast and to high molecular weights of polymacromonomers. However, as some amounts of reactive groups can be trapped at the same time in the hydrophilic core they polymerise slower as their local concentration is relatively low (relatively long poly(glycidol) chains). As the result product of lower molecular weight is formed.

Additionally, it was noticed that as the concentration of macromonomer upon polymerisation decreases the amount of the low molecular weight polymacromonomer fraction decreases (see Figure 6.41. The decrease of the concentration probably enhance formation of the loops by poly(glycidol) chain what leads to increase of concentration of double bonds at the border of core and shell of the micelle. As the result less reactive groups are trapped in the hydrophilic poly(glycidol) core, what also explains the fact that the molecular weights of polymacromonomers at lower concentrations are higher. However, that are only speculation which were not confirmed.

6.2.5. Separation of the polymacromonomer from unreacted oligomer

In order to separate the unreacted macromonomer from the polymerisation product, the reaction products were fractionated by methods described earlier (dialysis or precipitation). In all methods two fractions were separated: a high molar mass fraction, the polymacromonomer, and low molar mass fraction, consisting of the unreacted oligomer. The efficiency of the fractionation was proved by size exclusion chromatography. The chromatograms of purified polymacromonomers are presented in Figure 6.42.

a) Selective precipitation of polymacromonomer dissolved in methanol using acetone as precipitant



b) Dialysis in methanol from the membrane with an exclusion limit 50 000 g/mol

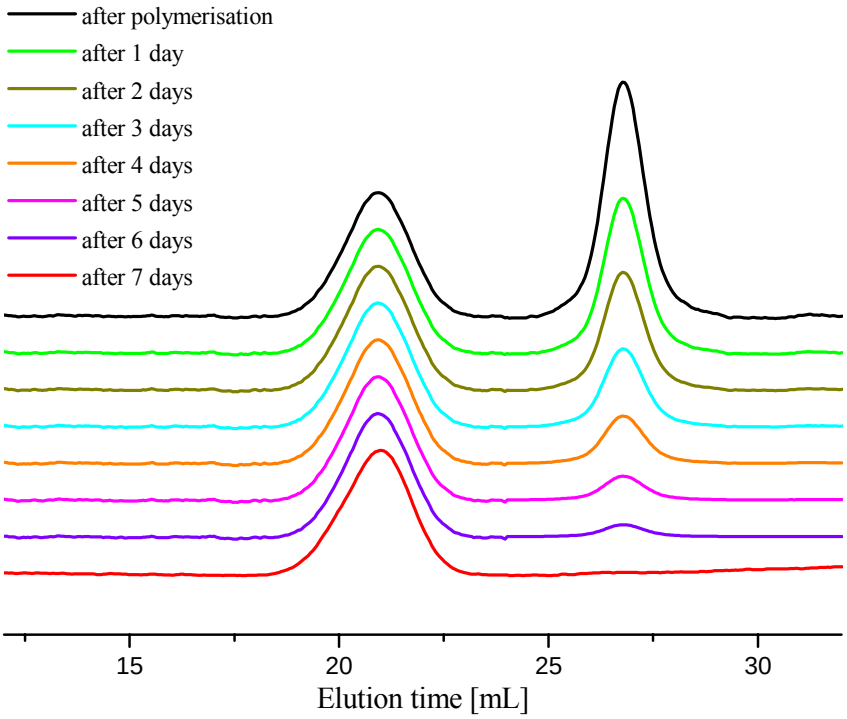


Figure 6.42. Purification of polymacromonomers by selective precipitation (a) and by dialysis in methanol (b); polymacromonomer of M_n = 505 000 g/mol obtained upon polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St.

The *SEC* data confirmed that efficient separation was achieved for all kinds of synthesised polymacromonomers in both used methods. In the separation by selective precipitation or precipitation to water polymacromonomers were obtained with the purity equal 95 % when by dialysis even 100% purity of the product was achieved.

Additionally, in some cases the separation of polymacromonomers by dialysis led to decrease of dispersity indices as polymacromonomers of low molecular weight fraction were separated together with unreacted residue.

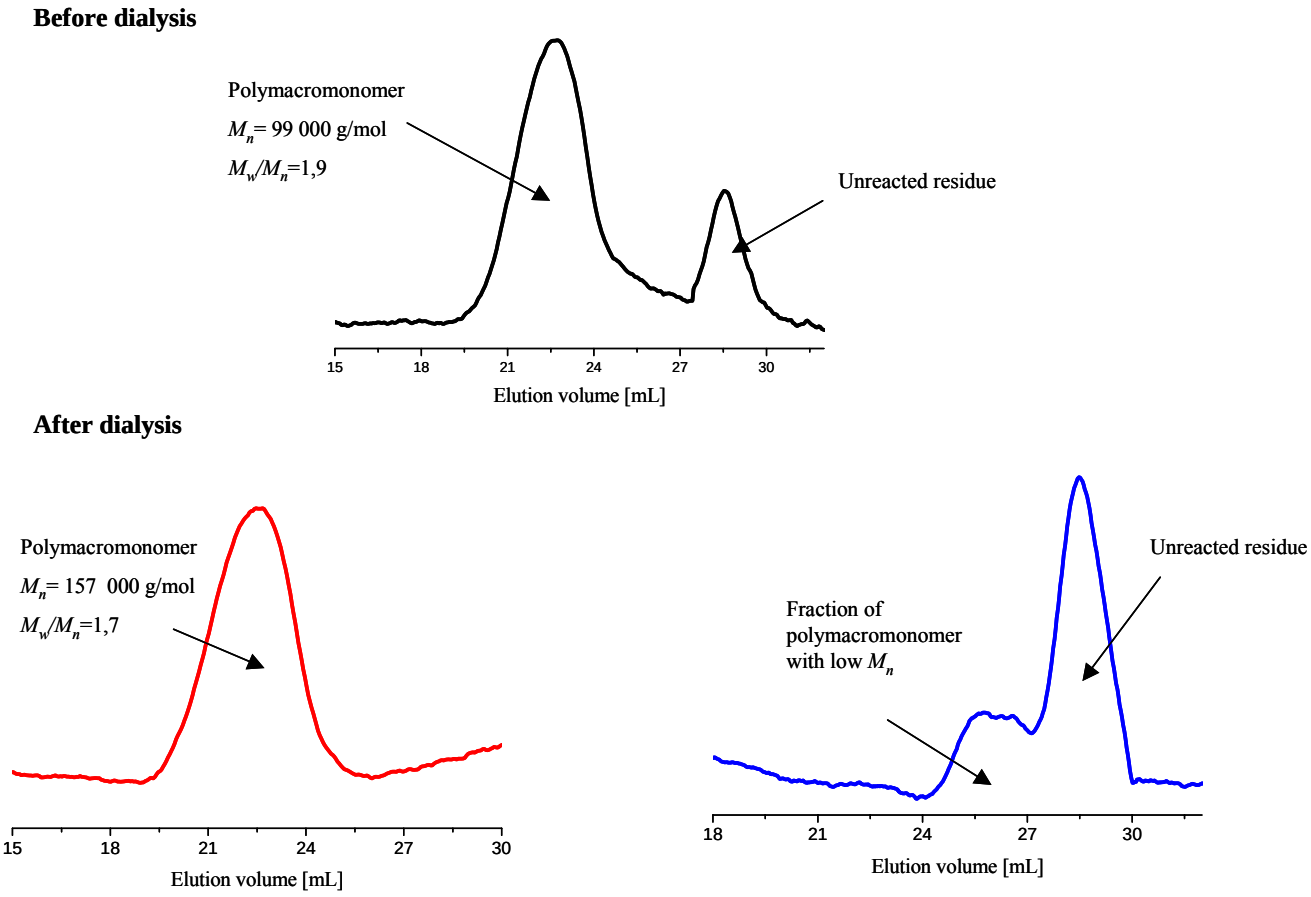


Figure 6.43. The example of decrease of dispersity index of polymacromonomer upon dialysis in methanol from the membrane with an exclusion limit 50 000 g/mol.

It was attempted to polymerise the separated low molecular fraction separated from the after polymerisation mixture, however, no conversion was obtained. In the ^{1}H NMR spectra of this fraction no signals of the double bond protons were observed (Figure 6.44.).

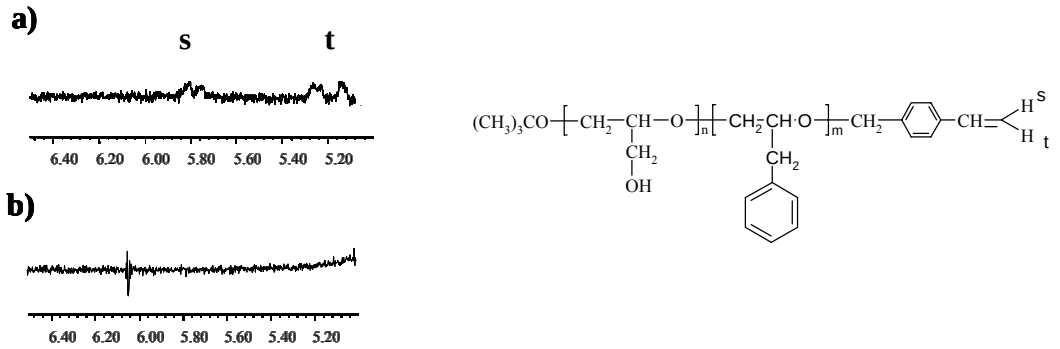


Figure 6.44. Part of ^{1}H NMR spectrum ($CDCl_3$, 300MHz) of:
a) the macromonomer PGl_{52}-*b*-$PGlPhE_8$-St before polymerisation,
b) low molar mass fraction separated from the reaction mixture after the polymerisation.

In the Figure 6.45 *MALDI-TOF-MS* spectra of the macromonomer PGl_{52}-*b*-$PGlPhE_8$-St before polymerisation and oligomer separated from the reaction mixture after the polymerisation are presented. The conversion of the functionalized macromonomer in that polymerisation was estimated to 97 %.

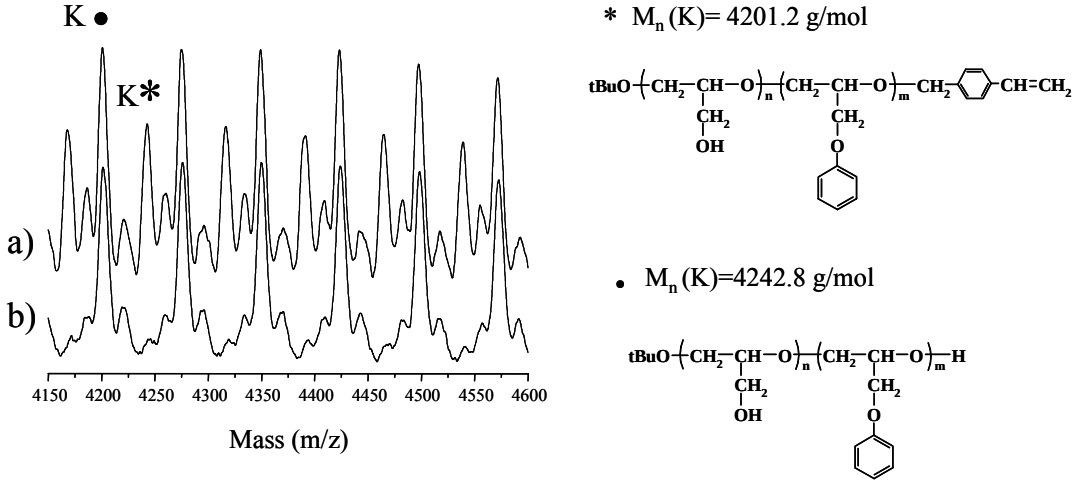


Figure 6.45. *MALDI-TOF-MS* spectrum of:
a) the macromonomer PGl_{52}-*b*-$PGlPhE_8$-St before polymerisation
b) low molar mass fraction separated from the reaction mixture after the polymerisation.

In the *MALDI-TOF-MS* spectra of separated oligomer fraction only one distribution can be found. The second distribution deriving from functionalized macromonomer (having vinyl benzyl end group) visibly disappeared what can be seen in the Figure 6.45. A reason for the apparent incomplete conversion of macromonomers is therefore as was expected the lack of the vinyl benzyl reactive groups in the molecule.

6.2.6. Properties of obtained polymacromonomers

The homopolymerisation of macromonomers provided a series of regular comb polymers. The polymerisation of hydrophilic macromonomers of poly(glycidol) bearing vinylbenzyl group (PGl-St) resulted in the hydrophilic polymacromonomer as presented in Figure 6.46. The main chain of such polymacromonomer constituted poly(styrene) substituted in *p*- position with poly(glycidol) chain.

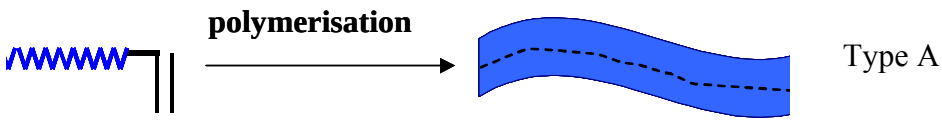


Figure 6.46. Homopolymerisation of PGl-St macromonomers.

The formation of main chain was visible in ^{1}H NMR. In the region of 5 - 8 ppm the signal deriving from protons situated at double bonds disappeared, where the one deriving from aromatic ring of poly(styrene) appeared.

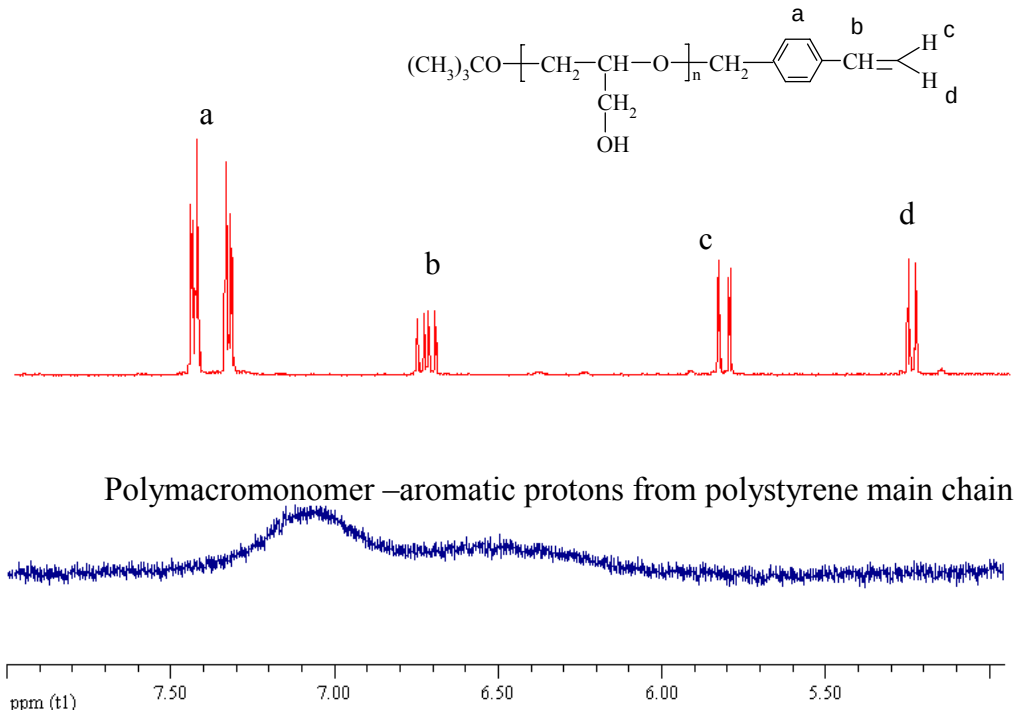


Figure 6.47. Part of the ^{1}H NMR spectra of macromonomer and polymacromonomer obtained from PGl_{55}-St.

On the other side, the homopolymerisation of block macromonomers PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St resulted in the core shell structures as presented in Figure 6.48. However, the properties of obtained brush structures were depended not only on the chemical composition of the arms but also on the relative arrangement of the blocks in the polymer molecule.

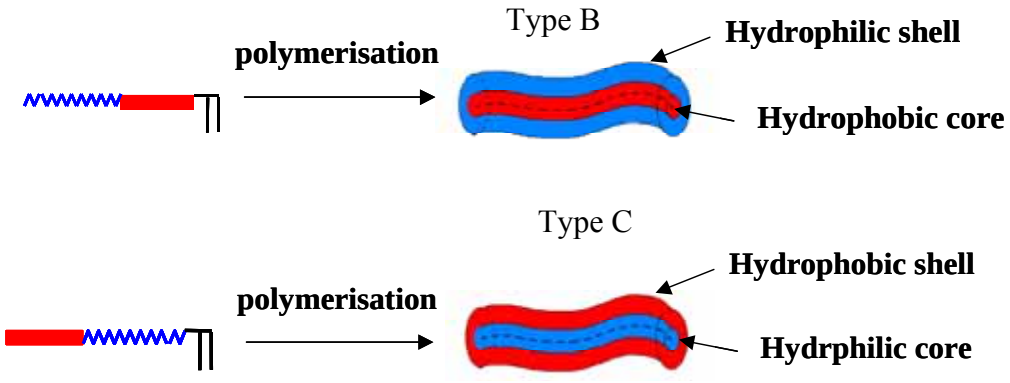


Figure 6.48. Homopolymerisation of amphiphilic macromonomers, PGl-*b*-PGlPhE-St and PGlPhE -*b*-PGl-St.

In Figure 6.49. the spectra of PGl-*b*-PGlPhE-St and of polymacromonomer obtained from this macromonomer (after removal of unreacted oligomer) in DMSO, which is a good solvent for both blocks, are presented.

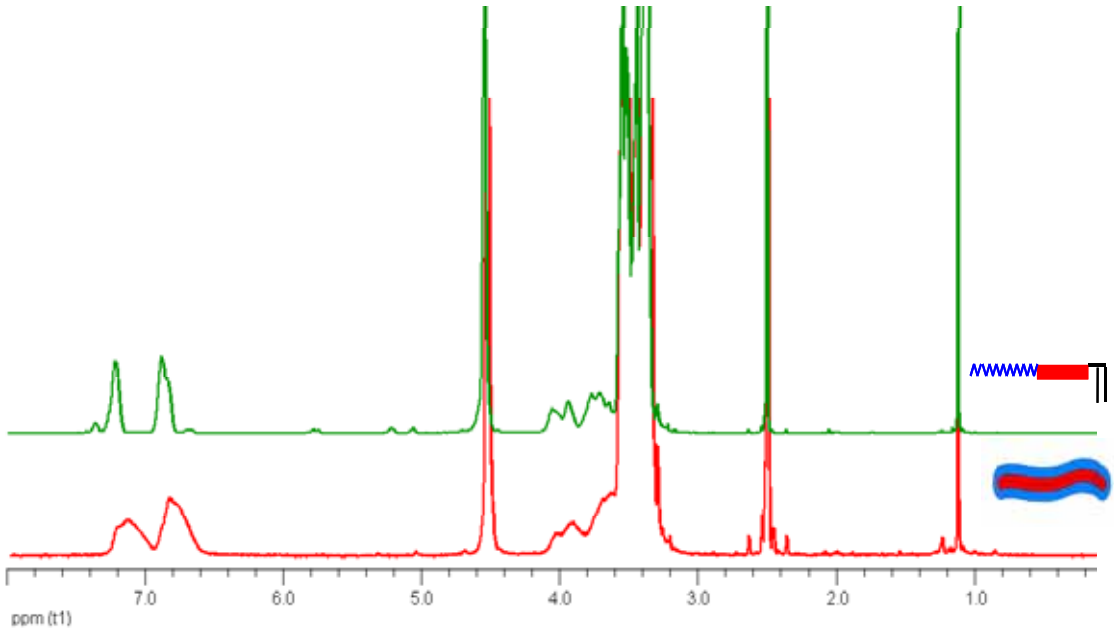


Figure 6.49. ^{1}H NMR spectra of macromonomer and polymacromonomer obtained from PGl-*b*-PGlPhE-St in DMSO-d_6.

In DMSO groups of signals deriving from both blocks forming polymacromonomer are visible. However, as it can be seen the peaks deriving from poly(phenyl glycidyl ether) are much broader in the polymacromonomer structure in comparison to signals observed for macromonomer PGl-*b*-PGlPhE-St. Such behaviour was already observed for branched polymers and is the result of the highly crowded structure of the polymer. The poly(phenyl glycidyl ether) forms the core of the brush and its mobility is suppressed, what results in broadening of the peak.

The obtained polymacromonomers in contrast to macromonomers used for their preparation did not show amphiphilic properties. When the hydrophilic blocks formed the shell the polymacromonomer was well soluble in water and polar solvents like methanol, but insoluble in THF. However, in the opposite case when short hydrophobic blocks constituted the shell the polymacromonomer remained soluble in THF however become completely insoluble in water. This was rather surprising as this polymacromonomer was in 75 wt-% built of hydrophilic poly(glycidol). The properties of polymacromonomers seems to be determined by the properties of shell i.e. the blocks forming the outer part of the brush. The composition of the macromonomer seems to be not that important as even short block of the poly(phenyl glycidyl ether) influenced the properties of polymacromonomer considerably.

Figure 6.50 presents a ^{1}H NMR spectrum of polymacromonomer in deuterated water, which is a good solvent for poly(glycidol), but poor solvent for the poly(phenyl glycidyl ether). The signals of the shell are readily observed indicating an extended conformation, while no signals of the hydrophobic polymer are observed, implying the complete collapse of the poly(phenyl glycidyl ether) forming core.

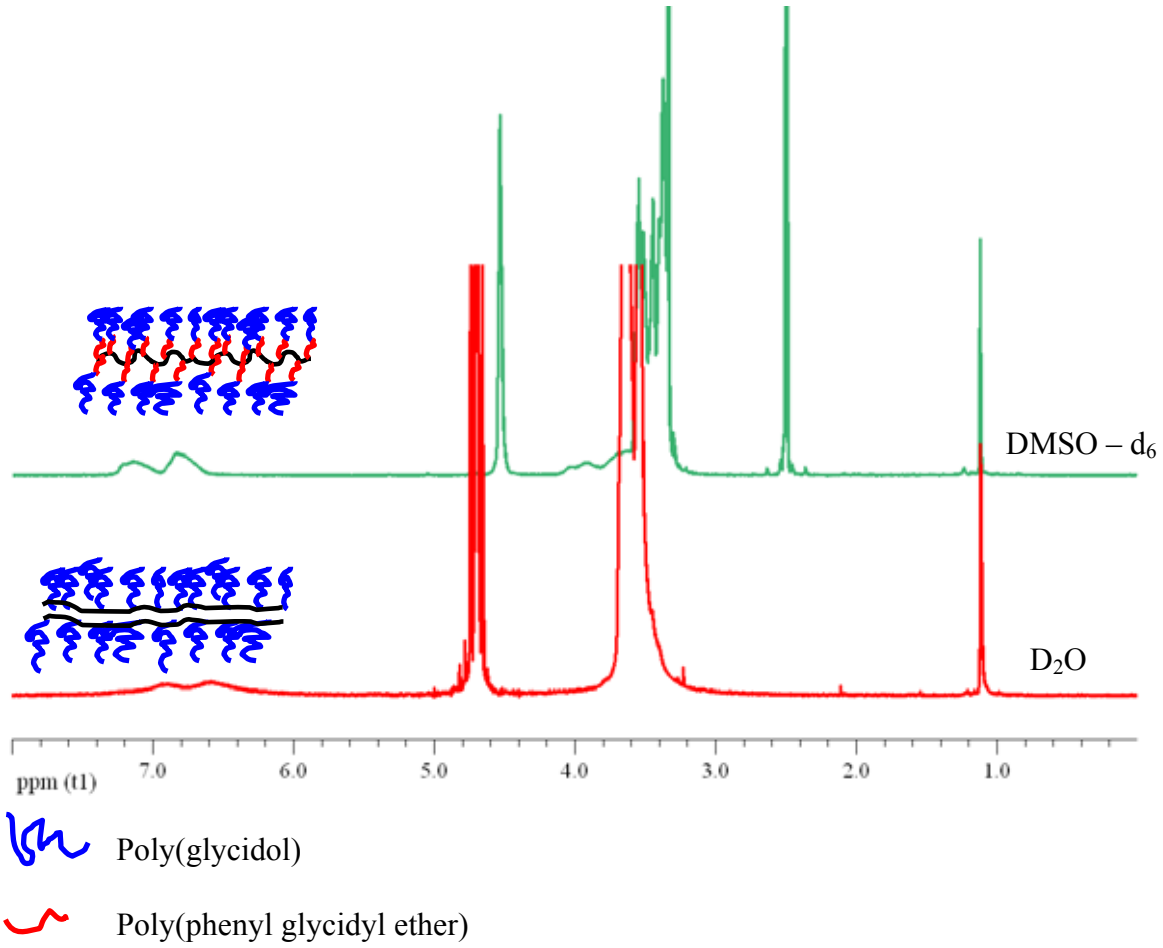


Figure 6.50. The ^{1}H NMR specta of polymacromonomer obtained from PGl-*b*-PGlPhE-St in deuterated water and DMSO-d_6.

In the case of polymacromonomer with the hydrophobic shell the spectra made in chloroform showed suppression of the peaks from poly(glycidol) blocks. However, as the peaks of main chain from poly(glycidol) and poly(phenyl glycidyl ether) overlap in the region 3,2-4,0 ppm it was not so well visible as in the previous case and are not presented.

6.2.7. Properties of polymacromonomers in solid state

As was discussed in literature review almost all branched polymers exhibit glass transition, although its nature is not exactly known. Therefore it was decided to look into the thermal behaviour of the obtained polymacromonomers using differential scanning calorimetry.

The T_g thermograms for all obtained types of polymacromonomers with similar molecular weight are presented in Figure 6.51.

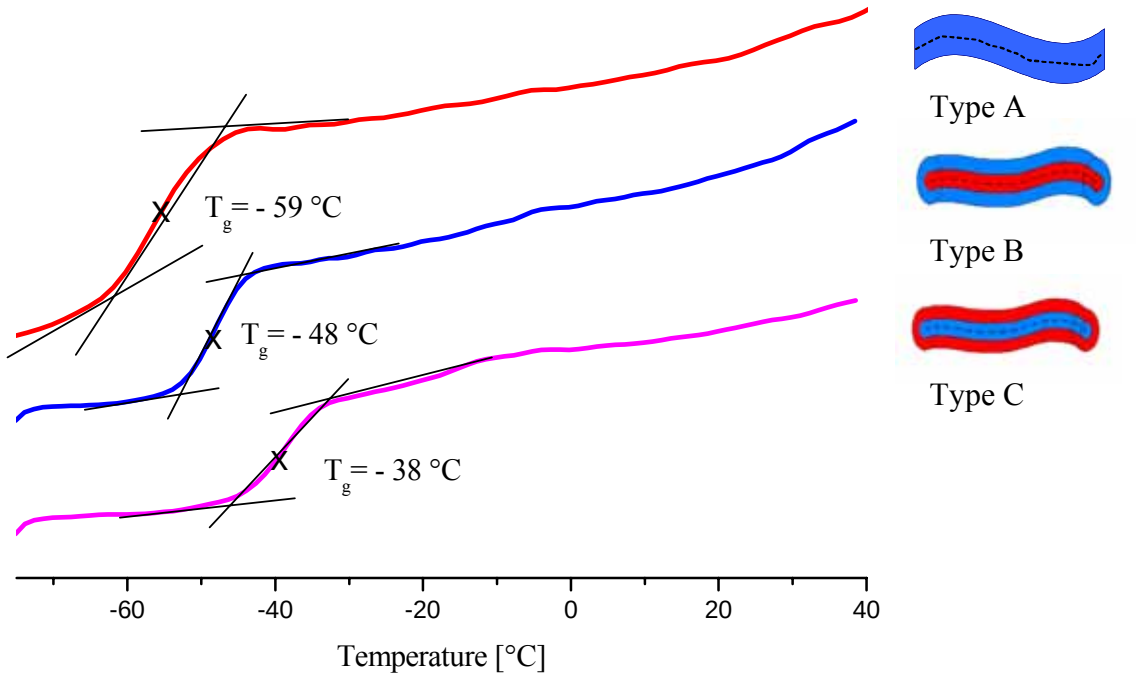


Figure 6.51. Thermograms of all types of obtained polymacromonomers; type A M_n = 157 000 g/mol, type B M_n = 210 000 g/mol, type C M_n = 250 000 g/mol

As it can be seen all investigated polymacromonomers showed single T_g. The transition of polymacromonomer appeared in the region of the transition of the macromonomer used for polymerisation (see Table 6.5.). However, in case of block polymacromonomers the T_g were few degree lower (3-4°C) then that of macromonomers used for preparation.

Generally, the T_g was found to increase with increase of the molecular weight of polymacromonomer [154]. Thus, the polymacromonomers of different molecular weight obtained from PGlPhE$_8$-*b*-PGl$_{52}$-St were investigated. However, in contrast to expectation the measured values of T_g presented in Table 6.11. were not influenced by the M_n of polymacromonomer (in the investigated range).

Table 6.11. T_g of polymacromonomers with different molecular weight obtained from PGlPhE$_8$-*b*-PGl$_{52}$-St (type C).

Sample	T_g [°C]
M_n = 105 000 g/mol	-39
M_n = 320 000 g/mol	-39
M_n = 500 000 g/mol	-38

Hence, it seems that the only factor influencing the T_g of polymacromonomers seems to be the composition of the branches, while the arrangements of the blocks or the molecular weight of polymacromonomer do not influence the transition. It seems that the glass transition corresponds to the relaxation of the side chains of the polymacromonomer, what was rather unexpected.

6.2.8. Adsorption of polymacromonomers from solutions

The adsorption of polymacromonomers on the surface was studied from DMSO which is a common solvent of all types of obtained polymacromonomers. The adsorption on two types of surfaces was examined: the hydrophobic surface of silica and hydrophilically modified silica surface. The *AFM* pictures of polymacromonomers adsorbed on hydrophilic surface are presented in Figure 6.52 and 6.53.

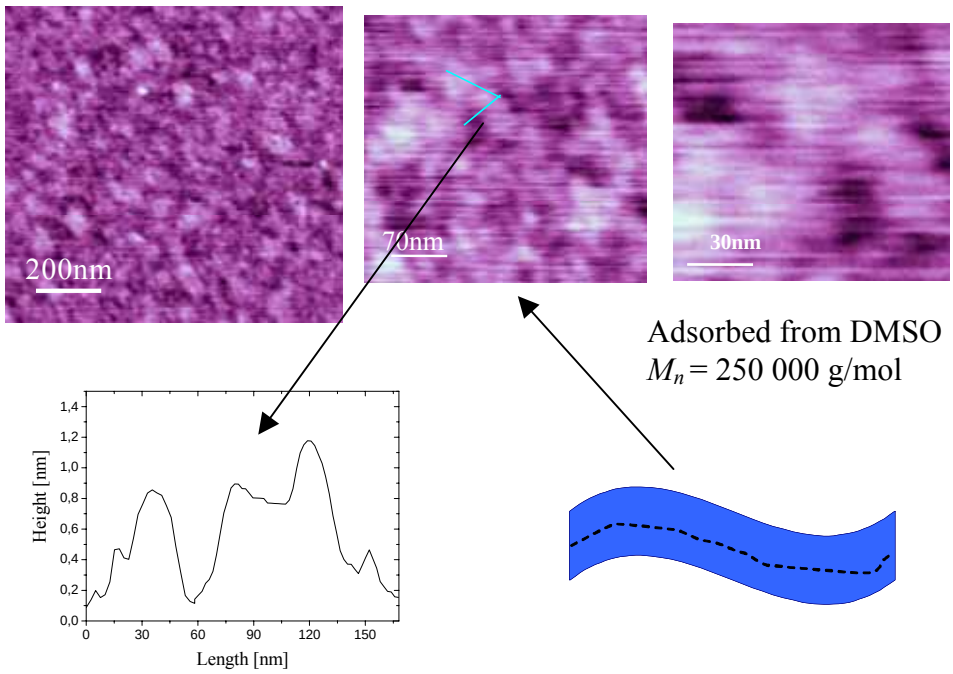


Figure 6.52. *AFM* pictures of adsorbed from DMSO polymacromonomer of type A (from PGl_{55}-St), C=1 g/L.

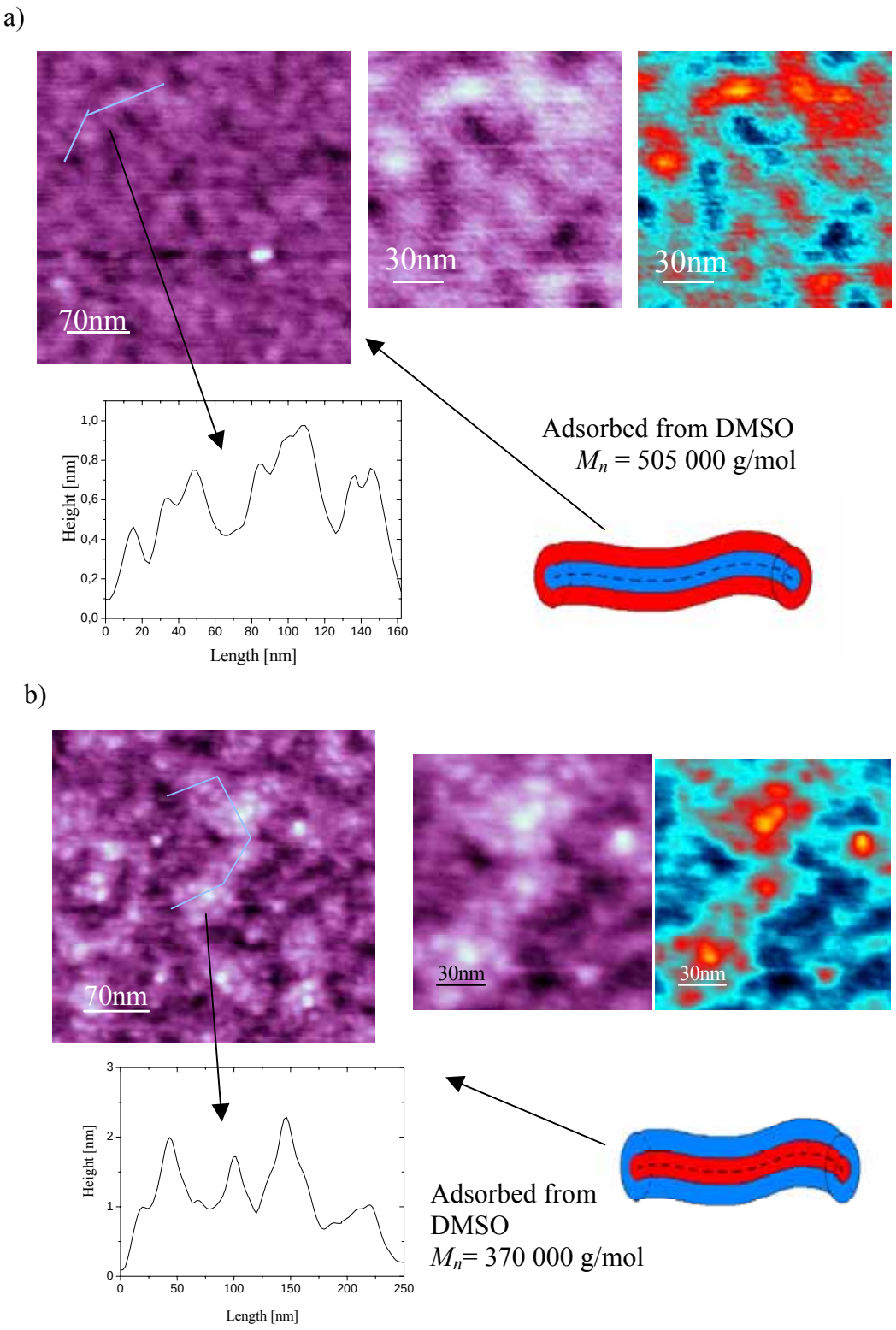


Figure 6.53. *AFM* pictures of adsorbed from DMSO block polymacromonomers of type C (from PGlPhE$_9$-*b*-PGl$_{54}$-St) (a) and type B (from PGl$_{52}$-*b*-PGlPhE$_8$-St) (b); C = 1 g/L.

As it can be seen (especially for core-shell structures) the polymacromonomers do not adsorb evenly on the surface, but form a spherical micellar shapes.

In Figure 6.54. the thickness of the layer of the adsorbed polymacromonomers on examined surfaces is presented.

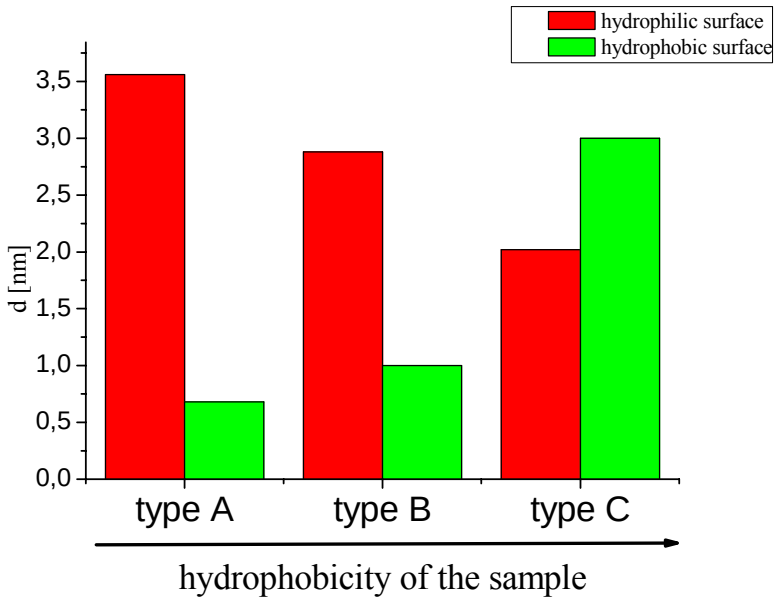


Figure 6.54. The thickness of the adsorbed polymacromonomer layer on hydrophilic and hydrophobic surface of modified silica wafer.

It can be seen that as the hydrophobicity of the polymacromonomer was increasing the amount of the polymacromonomer adsorbed on the hydrophilic surface was decreasing. Thus, the highest thickness of film was observed for polymacromonomers obtained from PGl-St macromonomer. However, surprisingly the polymacromonomer with hydrophobic shell also adsorbed on the hydrophilic surface. The poly(glycidol) blocks placed in the core of the polymacromonomer probably interacted with the surface in the way presented in Figure 6.55.

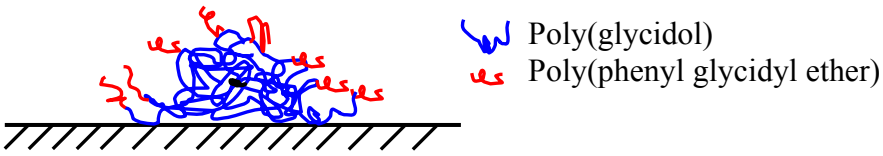


Figure 6.55. Adsorption of polymacromonomer of type C (hydrophobic shell) on hydrophilic surface.

The opposite tendency was observed upon adsorption of polymacromonomers on the hydrophobic surface, while the highest adsorption was observed for the most hydrophobic polymacromonomer with poly(phenyl glycidyl ether) shell. The amount of adsorbed polymacromonomer was similar for polymacromonomers A and B, however, much lower

then for C. That polymacromonomers are strongly hydrophilic so their adsorption on the hydrophobic surface was rather unexpected. Nevertheless, it should be remembered that at the shell of this polymacromonomers are concentrated hydrophobic *t*-butyl groups from initiator of anionic polymerisation and probably they are responsible for the adsorption of that polymacromonomers.

6.2.9. AFM study of polymacromonomers

In order to visualize the single molecules of polymacromonomers by *AFM* dilute solutions of the synthesised polymers in DMSO were spin-coated on mica. Using such procedure monomolecular films were obtained. The obtained AFM pictures are presented in Figure 6.56.

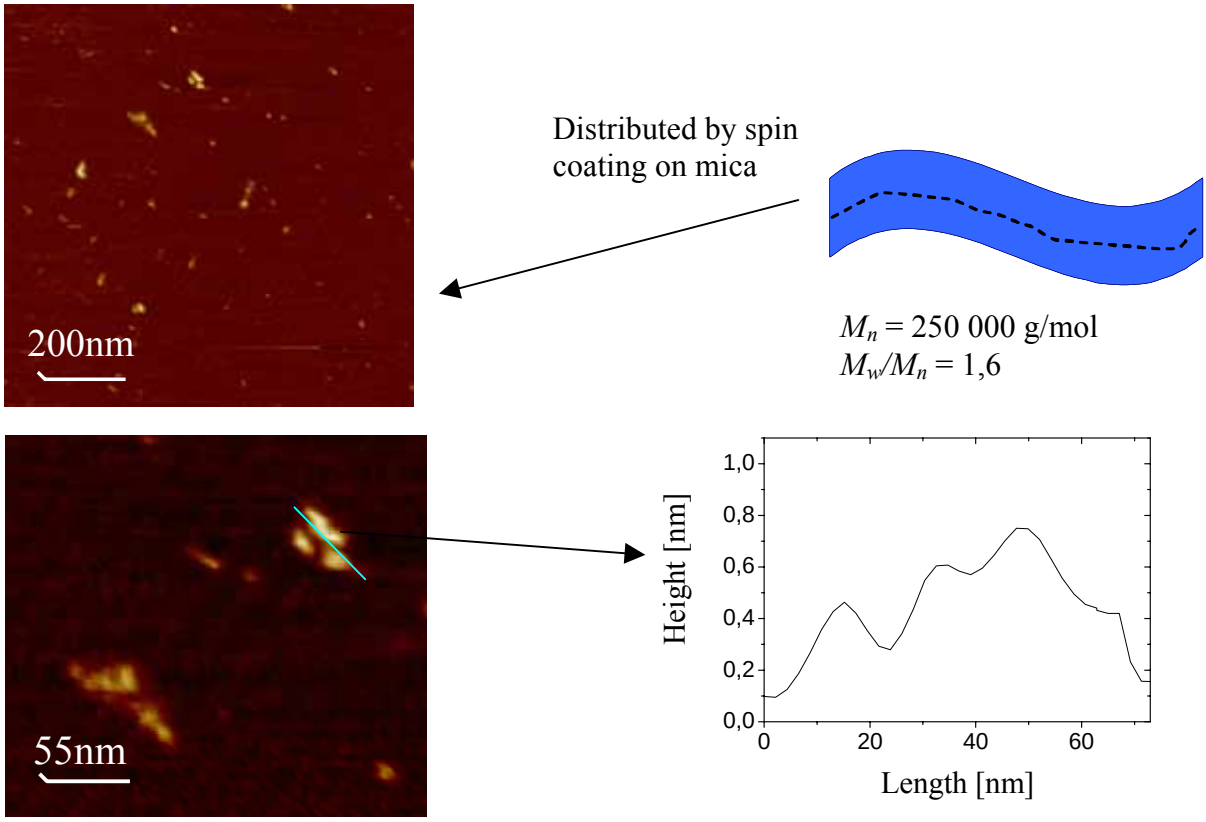


Figure 6.56. *AFM* picture of polymacromonomers type A (from PGl_{55}-St) distributed on mica by spin coating; C = 0,05 g/L.

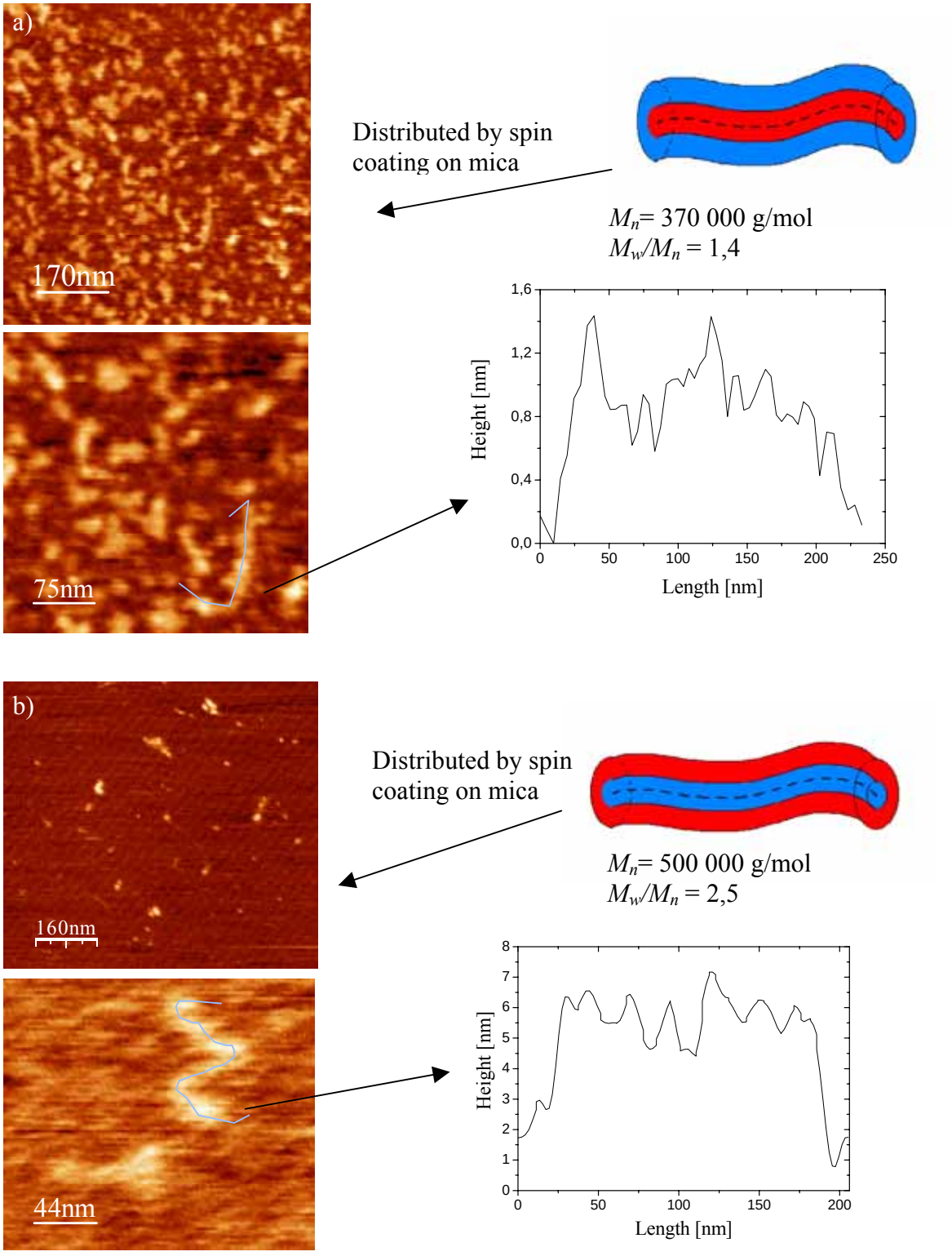


Figure 6.57. *AFM* picture of block polymacromonomers distributed on mica by spin coating, type B (from PGl_{52}-*b*-$PGlPhE_8$) (a) and type C (from $PGlPhE_8$-*b*-PGl_{53}-St) (b); C = 0,05 g/L.

In all cases, *AFM* revealed individual molecules lying flat on the substrate. However, as the polydispersity of the samples was relatively high in all sample rod-like as well as star-like molecules can be found.

6.3. Synthesis of temperature sensitive polymacromonomers

It was shown in the literature that the temperature sensitivity of polymers can be induced by modification of hydroxyl groups of polymers [241, 244]. For the poly(glycidol)s of different architectures (linear and grafted) the cloud point of the final product was controlled by the change of the degree of esterification in the range of 30-90% [241]. The replacement of the part of the hydroxyl groups with hydrophobic ester groups led to copolymers which exhibited the cloud point in water solutions varying from 4 to 100 °C.

The same idea was applied to the synthesis of temperature sensitive poly(glycidol)-based compact, highly dense polymacromonomers. However, two ways of synthesis were applied:

- Preparation of temperature sensitive macromonomers followed by their polymerisation to temperature sensitive polymacromonomers;
- Modification of hydroxyl groups of polymacromonomers obtained by polymerisation of poly(glycidol)-based macromonomers.

Depending on the applied synthetic route different distribution of the hydrophobic acetate groups is expected. In the first synthetic way the distribution of the temperature sensitive groups in the structure of the macromonomer will be statistical. Polymerisation of such macromonomer should also yield polymacromonomers with randomly distributed temperature sensitive groups as presented in Figure 6.58.

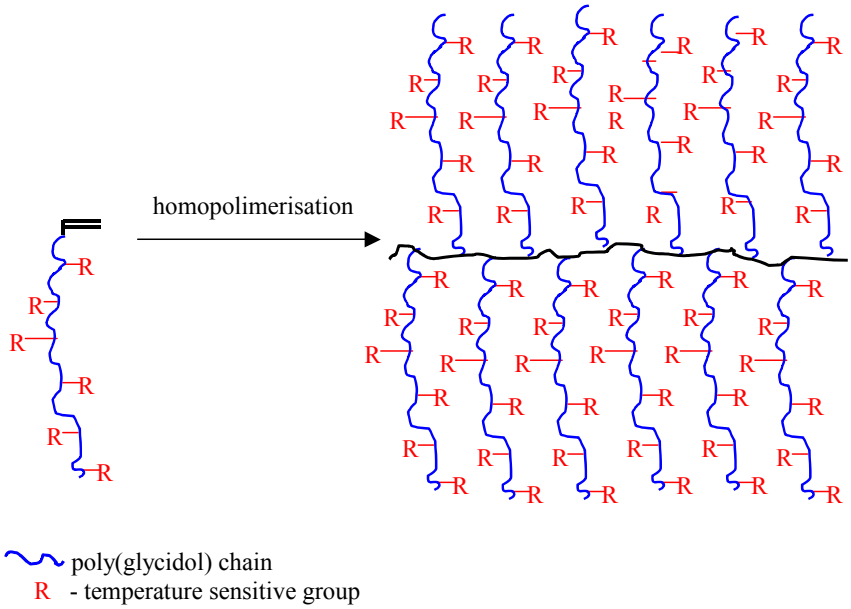


Figure 6.58. Preparation of temperature sensitive polymacromonomers by polymerisation modified of macromonomers.

The second approach including modification of already prepared polymacromonomers should bring polymers, where the distribution of the temperature sensitive groups will not be statistical. The structure of the polymacromonomer is much more compact then the structure of the linear chain. Therefore the outer units of polymacromonomer are more accessible to the esterification then the one in the core of highly branched structure. As the result the temperature sensitive acetate units are likely to be concentrated on the outer shell as presented in Figure 6.59.

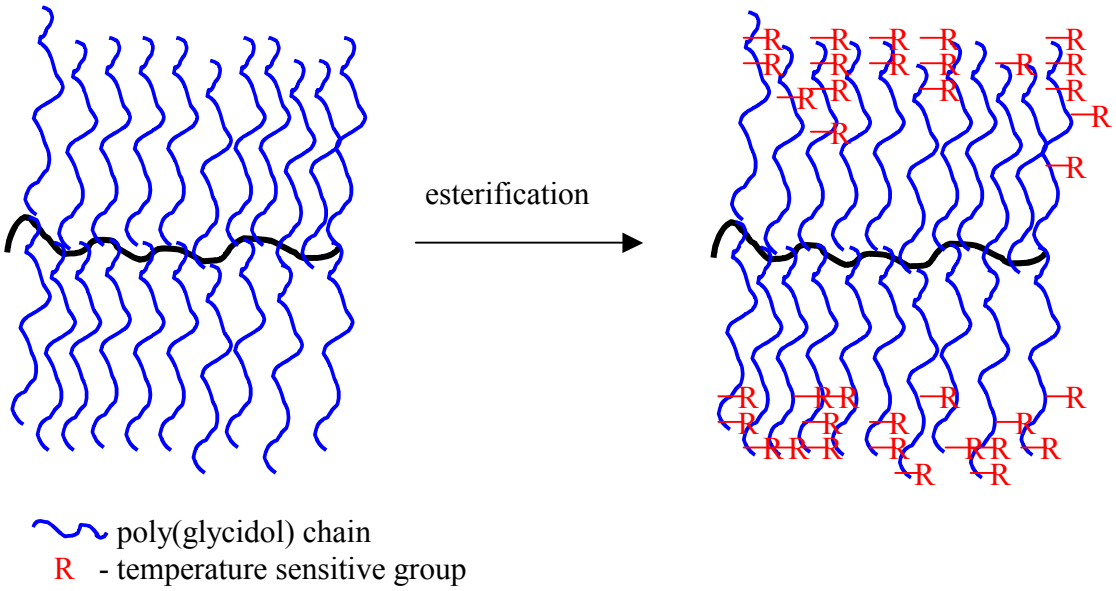


Figure 6.59. Preparation of temperature sensitive polymacromonomers by esterification of hydroxyl groups of polymacromonomers.

The polymacromonomers with the same overall content of the ester groups but prepared by this different synthesis rout were expected to show different cloud point values. As the outer sphere of branched polymer interacts with the solvent and with other molecules the polymacromonomer obtained by modification of polymacromonomers should appear to be more hydrophobic then the linear one and show lower cloud points.

6.3.1. Preparation of temperature sensitive polymacromonomers from macromonomers

As it was shown in previous chapters the polymacromonomer obtained by polymerisation of $PGlPhE_8$-*b*-PGl_{53}-St is insoluble in water. Thus, only PGl_{55}-St and PGl_{52}-*b*-$PGlPhE_8$-St, which polymerisation results in water soluble polymacromonomers were used for preparation of temperature sensitive macromonomers.

The degree of substitution of hydroxyl groups of poly(glycidol) was varied by the proper choice of the stechiometry of the mixture used for esterification. The successful introduction of acetate groups to the poly(glycidol) chain in the case of both macromonomers was confirmed by ^{1}H NMR. The new peak deriving from methyl groups from acetate appeared at 2,1 ppm, where methylene groups from the backbone were detected as doublet at 4,0 and 4,2 ppm, what can be seen in the Figure 6.60.

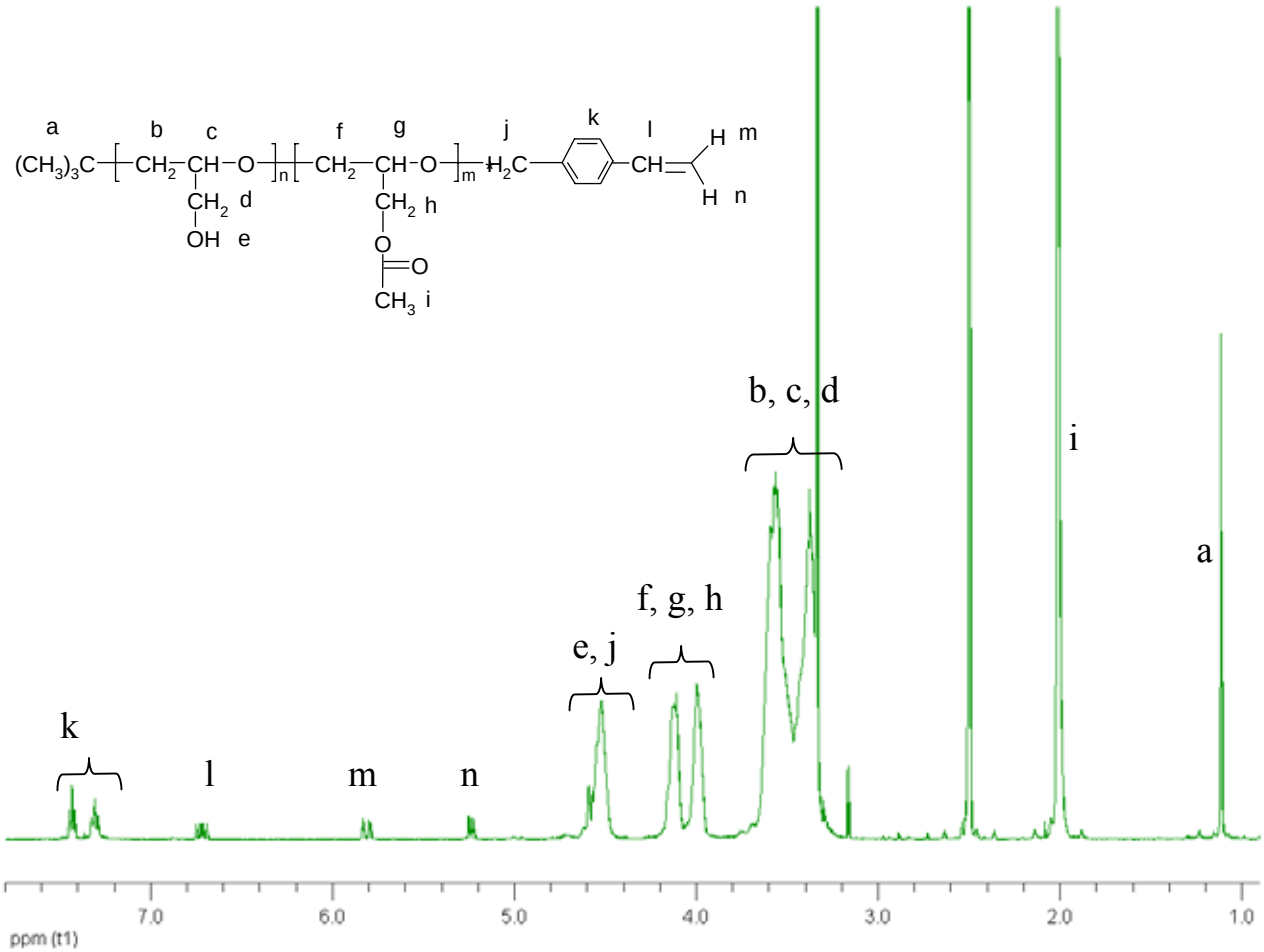


Figure 6.60. The spectra of temperature sensitive macromonomer in DMSO-d_6 obtained from PGl_{55}-St (sample PGl_{55}-St-3 see Table 6.12.), the calculated degree of esterification 51 %.

The degree of esterification was determined from ^{1}H NMR spectra as the ratio of integral of methyl protons from acetate group and the integral of protons from poly(glycidol) main chain in the region 3,4-3,8 ppm. The results are presented in Table 6.12.

Table 6.12. Esterification of PGl_{55}-St macromonomer.

Sample	Degree of esterification [%]		T_c [°C]
	targeted	obtained	
PGl_{55}-St-1	55	42	Soluble in water from 1 to 100 °C
PGl_{55}-St-2	60	48	79
PGl_{55}-St-3	65	51	50
PGl_{55}-St-4	70	55	37
PGl_{55}-St-5	75	62	20
PGl_{55}-St-6	85	75	5
PGl_{55}-St-7	90	82	water insoluble
PGl_{52}-*b*-$PGlPhE_8$-St-1	70	53	38

As it can be seen the esterification of poly(glycidol) macromonomers resulted in the series of temperature sensitive macromonomers. In each case the obtained degree of esterification was about 15 % lower then the targeted value, nevertheless it could be well controlled. However, in the case of macromonomers obtained after modification of PGl_{52}-*b*-$PGlPhE_8$-St the *SEC* measurements showed two peaks as it can be seen in the Figure 6.61b. The first was deriving from temperature sensitive macromonomer, where second was assigned to the polymacromonomer. It means that although no radical initiator was introduced to the system in the applied esterification conditions macromonomer polymerises spontaneously to reach about 10 % of conversion. The further experiments were than stopped as the synthesis could not be controlled. In the case of esterification of PGl_{55}-St such behaviour was not observed and only peak deriving from esterified macromonomer was detected (Figure 6.61 a).

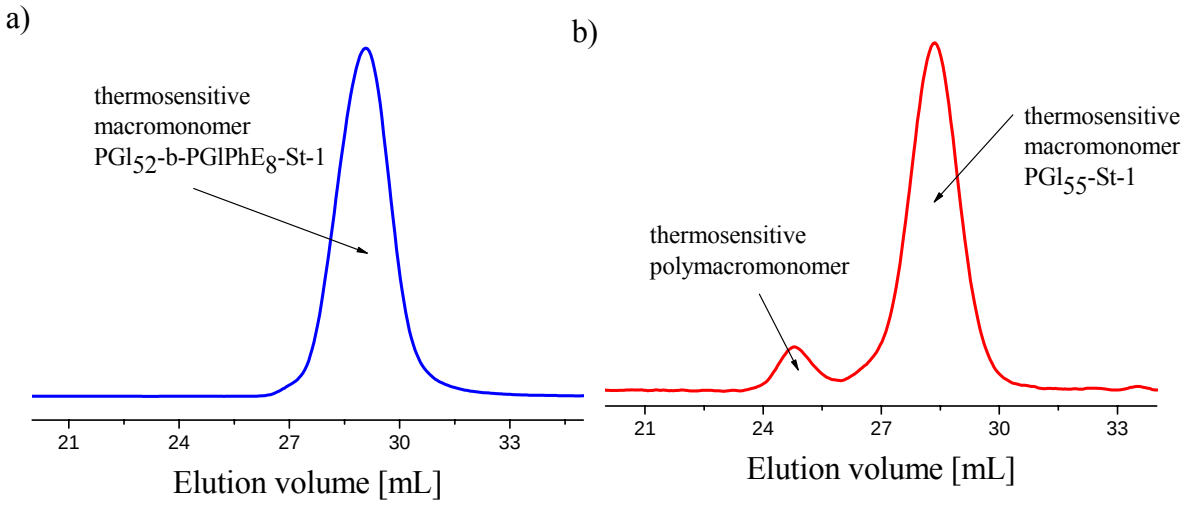


Figure 6.61. *SEC* traces of temperature sensitive macromonomers: (a) PGl_{55}-St-1 (b) PGl_{52}-*b*-$PGlPhE_8$-St-1.

The measurements of the cloud point of temperature sensitive macromonomers obtained from PGl_{55}-St were performed at the concentration of 5 g/L using *UV-VIS* spectrometery. The transition temperature was estimated graphically from the plot of the absorption at λ = 400 nm versus temperature. The phase separation temperature was understood as projection of crossover point on "X" axis, between of the baseline of absorbance and the extrapolated line of the curve slope, what is schematically presented in Figure 6.61.

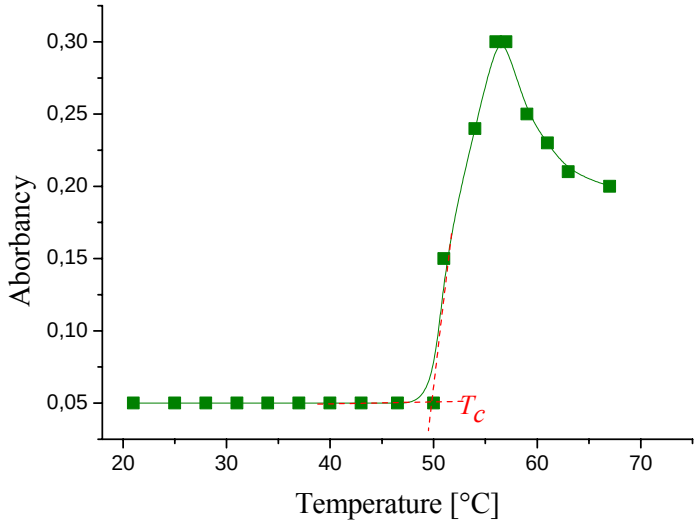


Figure 6.62. The *UV-VIS* plot of the absorption at λ = 400 nm versus temperature for PGl_{55}-St-2, c = 5 g/L.

Additionally, as it can be seen at the temperature interpreted as the cloud point the distinct increase of the absorbency appears, what is a result of the increase of the turbidity of the sample. However, above T_c the absorbency versus temperature curve for these macromonomers suffered a downward trend. It seems to be the effect of the further aggregation of the macromonomers, which gradually precipitated from the solution.

The increase of the esterification degree was accompanied by decrease of the T_c value. When more then 80 % of hydroxyl groups are esterified the polymers become insoluble in water.

The trials to polymerise obtained macromonomers were unsuccessful and temperature sensitive polymacromonomers were not obtained using that approach. As most of the synthesised temperature sensitive macromonomers was insoluble in water at 60 °C application of conventional radical polymerisation was impossible. From the other side, the *ATRP* of temperature sensitive macromonomers at 25 °C failed probably because of not enough purity of macromonomers, what was already observed before.

6.3.2. Modification of polymacromonomers to temperature sensitive brushes

The ^{1}H NMR confirmed successful introduction of acetate groups upon esterification of polymacromonomers of type A (obtained from PGl_{55}-St) and B (obtained from PGl_{52}-*b*-$PGlPhE_8$-St) with similar molecular weights. However, similarly as in case of modification of macromonomers the obtained degree of esterification was lower then targeted value as it can be seen in Table 6.13.

Table 6.13. Esterification of polymacromonomers of type A and type B.

Sample	Degree of esterification [%]		Sample	Degree of esterification [%]	
	targeted	obtained		targeted	obtained
Type A - 1	60	49	Type B - 1	60	49,6
Type A - 2	65	52	Type B - 2	65	53
Type A - 3	70	56	Type B - 3	70	59
Type A - 4	80	68	Type B - 4	80	69
Type A - 5	90	83	Type B - 5	90	86

The values of T_c measured by *UV-VIS* measurements at 5 g/L for the series of both types of polymacromonomers with different degree of esterification are presented in the Figure 6.63.

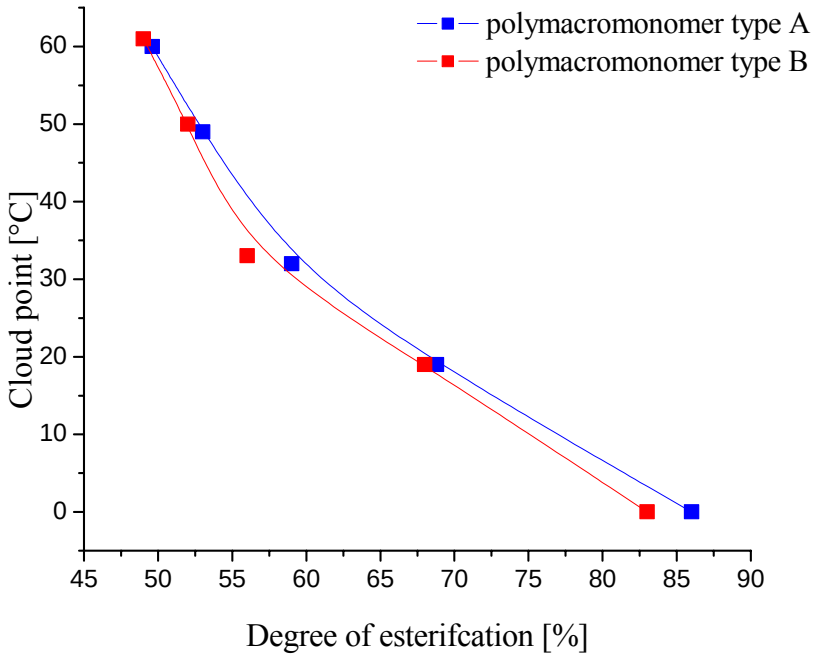


Figure 6.63. T_c of temperature sensitive polymacromonomers of type A (M_n= 250 000 g/mol) and core-shell polymacromonomer of type B (M_n= 280 000 g/mol) at c=5 g/L.

As it was expected the increase of the degree of esterification resulted in decrease of the T_c value. Additionally, for both type of polymacromonomers the same degree of esterification resulted in the same T_c value. It confirms that the outer part of the branched polymers is responsible for the interactions with the solvent. The presence of lack of the hydrophobic core does not influence the behaviour of temperature sensitive polymacromonomers in water.

The application of the second approach including the esterification of water soluble polymacromonomers resulted in the series of well-defined temperature sensitive polymacromonomers, where the T_c of the product can be controlled. The relatively little synthetic effort gives the poly(glycidol)-based polymacromonomers of T_c form 5 to 60 °C.

7. Summary

The aim of this work was the synthesis of hydrophilic macromonomers of glycidol (2,3-epoxypropanol) terminated with vinyl benzyl groups as well as of amphiphilic block macromonomers of glycidol and phenyl glycidyl ether terminated with vinyl benzyl group and their polymerisation. In the chapter 6: "Results and Discussion" the results of the experiments have been described and discussed in details and in this part will be briefly summarised.

The Synthesis of *α-t*-butoxy-*ω*-vinyl benzyl-poly(glycidol)-*block*-poly(phenyl glycidyl ether) (PGl-*b*-PGlPhE-St), *α-t*-butoxy-*ω*-vinyl benzyl-poly(phenyl glycidyl ether)-*block*-poly(glycidol) (PGlPhE-*b*-PGl-St) as well as homopoly(glycidol) macromonomers *α-t*-butoxy-*ω*-styrene-poly(glycidol) (PGl-St) under the described conditions was possible and led to defined macromonomers with narrow molar mass distributions and desired composition. Nevertheless, during the synthesis of macromonomers at the termination step the loss of polymerizable vinyl benzyl end group was observed leading to a decrease of the functionalisation of macromonomers to about 50 %.

The application of the ten-fold amount of terminating agent in respect to growing polymer chain allowed to increase the functionalisation of macromonomers to about 70 %. However, further increase of the amount of the terminating agent did not improve the results. The functionality of the macromonomers was also not increased by application of two step synthesis where as first the macroanion was terminated with water to give *ω*-hydroxyl poly(glycidol acetal) and then reacted according to Williamson's synthesis with excess of *p*-vinyl benzyl chloride. Thus, to the further experiments the samples being a mixture of nonfunctionalized oligomer and functionalized macromonomer were used.

All synthesised macromonomers showed amphiphilic properties and formed micelles in water. The critical micellization concentration of PGl_{55}-St was found on the level of 10 g/L. The introduction of hydrophobic spacer of poly(phenyl glycidyl ether) to the poly(glycidol) chain resulted in the district decrease of the critical micellization concentration as the values found for block macromonomers $PGlPhE_9$-*b*-PGl_{54}-St and PGl_{52}-*b*-$PGlPhE_8$-St were more then ten-times lower (0,6 and 0,8 g/L, respectively).

DLS measurements showed the formation of small, compact, monodisperse micelles by the block macromonomers, where the hydrodynamic radius was in the range of 10 nm. The core of the micelle was formed by in water insoluble poly(phenyl glycidyl ether), where poly(glycidol) formed the shell. In the case of PGl_{55}-St a bimodal distribution of the hydrodynamic radius was observed. The peak at 51 nm was assigned to the micelles formed by the macromonomer, where the peak at 1,5 nm derived from nonfunctionalized oligomers (unimer) unable to self-organization. In this case the core of micelles was formed by in water insoluble vinyl benzyl groups.

The formation of small well-defined narrow distributed opposite micelles (the poly(glycidol) core and poly(phenyl glycidyl ether) shell) in the case of both block macromonomers PGl_{52}-*b*-$PGlPhE_8$-St and $PGlPhE_8$-*b*-PGl_{53}-St was also observed in THF. The size of the micelles was smaller then in water ($R_h \approx 8$ nm).

The homopolymerisation of the studied macromonomers in water as well as in THF was distinctly influenced by occurrence of micellization.

Similarly as was observed for PEO macromonomers the homopolymerisation of all investigated types of macromonomers in water initiated with *AVA* was fast. After about 2 hours the conversion of macromonomers reached a constant value. The rate of polymerisation was extremely high in the case of PGl-*b*-PGlPhE-St, while the lowest value was observed for PGlPhE-*b*-PGl-St. The conversion of the substrate used for the reaction was not exceeding 70 %, whereas the actual conversion of the macromonomer in reaction mixture varied from 95 to 100 %.

Upon the polymerisation of these macromonomers in the mixture of water/benzene (10/1 v/v) initiated with *AIBN* for PGl-St and PGl-*b*-PGlPhE-St, the rate of polymerisation decreased about four-times in comparison to the polymerisation carried out in pure water. The introduction of benzene to the polymerisation system resulted in formation of the swollen micelles. The local concentration of the double bonds in the micelle core decreased by decreasing the reaction rate. Nevertheless, the conversion of these macromonomers remained unchanged and, similarly as in pure water, varied from 95 to100 %.

The different behaviour was noticed for $PGlPhE_8$-*b*-PGl_{53}-St. In the water/benzene mixture the R_P of polymerisation increased of 100 % in comparison to the polymerisation in pure water, what was accompanied by slight increase of macromonomer conversion (~ 5%). It seems, that the formation of swollen micelles enhanced the polymerisation or by the increase of the local concentration of vinyl benzyl reactive groups in the core of the micelle (the effect of formation of

the loop by poly(glycidol) chains) or by the increase of the solubility of the growing radical upon polymerisation.

As in the case of the PEO macromonomers [22], the degree of polymerisation of polymacromonomers was increasing with increased initial concentration of the macromonomers in the reaction mixture regardless of the polymerisation system or macromonomer type. In the case of PGl_{52}-*b*-$PGlPhE_8$-St and PGl_{55}-St the molecular weights of polymacromonomers obtained upon polymerisation in water were higher than that obtained upon polymerisation in the benzene/water mixture at the same concentration. The opposite effect was observed for $PGlPhE_8$-*b*-PGl_{53}-St, where the introduction of benzene to the polymerisation system slightly increased the *DP* of the polymacromonomer.

It seems that the intramicellar mechanism of the homopolymerisation of macromonomers in water is observed as in all cases above certain concentration (about 0,2 g/mL) *DP* of the products varied only moderately by the effect of macromonomer concentration.

The conditions of controlled polymerisation were found for PGl_{52}-*b*-$PGlPhE_8$-St macromonomer. The *ATRP* carried out in water using α-methoxy-ω-bromopropionate poly(ethylene oxide) as initiator and *Me_6TREN* as ligand gave polymacromonomers with the polydispersity of the products varying from 1,1 to 1,3. The M_n of polymacromonomer was well controlled by the change of the initiator/macromonomer ratio, however, only till 550 000 g/mol. Above this value the molecular weights of the products were much lower then targeted once while their polydispersities increased. It seems to confirm that the polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St proceeds in the core of the formed in water micelles with some additional non-organised macromonomers as was observed before. The intermicellar propagation do not occur. The conditions of *ATRP* for PGl_{55}-St and $PGlPhE_8$-*b*-PGl_{53}-St were not found.

As the *DLS* measurements showed formation of micelles in THF the polymerisation behaviour of block macromonomers was also studied in this solvent. The obtained results were in contrast to the results obtained upon polymerisation of these macromonomers in water. $PGlPhE_8$-*b*-PGl_{53}-St polymerised in THF more rapidly and to much higher molecular weights of polymacromonomers then PGl_{52}-*b*-$PGlPhE_8$-St. Moreover, in case of PGl_{52}-*b*-$PGlPhE_8$-St, the formed polymerisation product had very low molecular weight, lower then 50000 g/mol (DP $\approx$ 10) and was badly separated from the unreacted residue. Also upon

polymerisation of PGlPhE$_8$-*b*-PGl$_{53}$-St regardless from the concentration the bimodal products were obtained, however, with higher molecular weights.

The homopolymerisation of the synthesized poly(glycidol)-based macromonomers due to the not quantitive functionalisation led to the mixture of densely branched macromolecules and unreacted residue. In order to separate the unreacted macromonomer from the polymerisation product, the reaction products were fractionated by dialysis or precipitation. The efficiency of the fractionation proved by size exclusion chromatography was very high and the purity of the polymacromonomer varied from 95-100 %. It was attempted to polymerise the separated low molecular fraction separated from the after polymerisation mixture, however, no conversion was obtained.

The properties of the polymacromonomer depended on the type of the macromonomer used to polymerisation. The homopolymerisation of PGl-St resulted in the hydrophilic polymacromonomers with the poly(styrene) main chain and poly(glycidol) side chains, while in case of PGl-*b*-PGlPhE-St and PGlPhE-*b*-PGl-St core-shell structures were obtained. The obtained polymacromonomers in contrast to macromonomers used for their preparation did not exhibit amphiphilic properties. The behaviour of polymacromonomers was governed by the properties of the shell, i.e. the blocks forming the outer part of the brush. Thus, polymacromonomers obtained from PGl-*b*-PGlPhE-St, were soluble in polar solvents like methanol, or water, but insoluble in THF, whereas the polymacromonomers obtained from PGlPhE-*b*-PGl-St were insoluble in polar solvents, but soluble in THF.

The in pure water soluble polymacromonomers (without oligomer) obtained after polymerisation of PGl$_{52}$-*b*-PGlPhE$_8$-St and PGl$_{55}$-St were used for the preparation of temperature sensitive brushes, by esterification of the part of the hydroxyl groups of the polymacromonomer. The relatively small synthetic effort gave the poly(glycidol)-based polymacromonomers of T_c form 5 to 60 °C, where the T_c was varied by the change of the degree of esterification. The increase of the degree of esterification resulted in decrease of the T_c value. Additionally, for both types of modified polymacromonomers the same degree of esterification resulted in the same T_c value. It confirms that the outer part of the branched polymers is responsible for the interactions with the solvent. The presence of lack of the hydrophobic core does not influence the behaviour of temperature sensitive polymacromonomers in water.

8. Outlook

One of possible applications of synthesised macromonomers could be the synthesis of microspheres without emulsifiers or dispersants as poly(glycidol) macromonomers themselves act as surfactants. The resulting core-shell structures (emulsions or dispersions) would be stabilized against flocculation by soluble in water poly(glycidol) chains. Moreover, the presence of easy accessible hydroxyl groups offers the possibility to locate reactive groups or reactive sides i.e. enzymes, catalysts etc. in the structure of such prepared microspheres.

Another possibility is the modification of the surfaces by macromonomer technique. The *ATRP* of small monomers initiated from the surface, so called *grafting from* technique, is well-known method of preparation of polymer brushes with controlled molecular weight and molecular weight distribution [245-246]. Nevertheless, the polymerisation of macromonomers from the surface was not reported so far. However, by polymerisation of the obtained block macromonomers the core-shell tubes attached to the structure could be obtained. It can be expected that the cores of the formed by macromonomers in aqueous micelles will reach the surface and the attached to that surface initiators moieties will initiate the reaction. As the result of polymerisation of PGl-*b*-PGlPhE-St the core of the tube will be hydrophobic surrounded by the hydrophilic poly(glycidol) chains as is presented in the Figure 8.1., where the polymerisation of PGlPhE-*b*-PGl-St should give the tubes with hydrophobic shell.

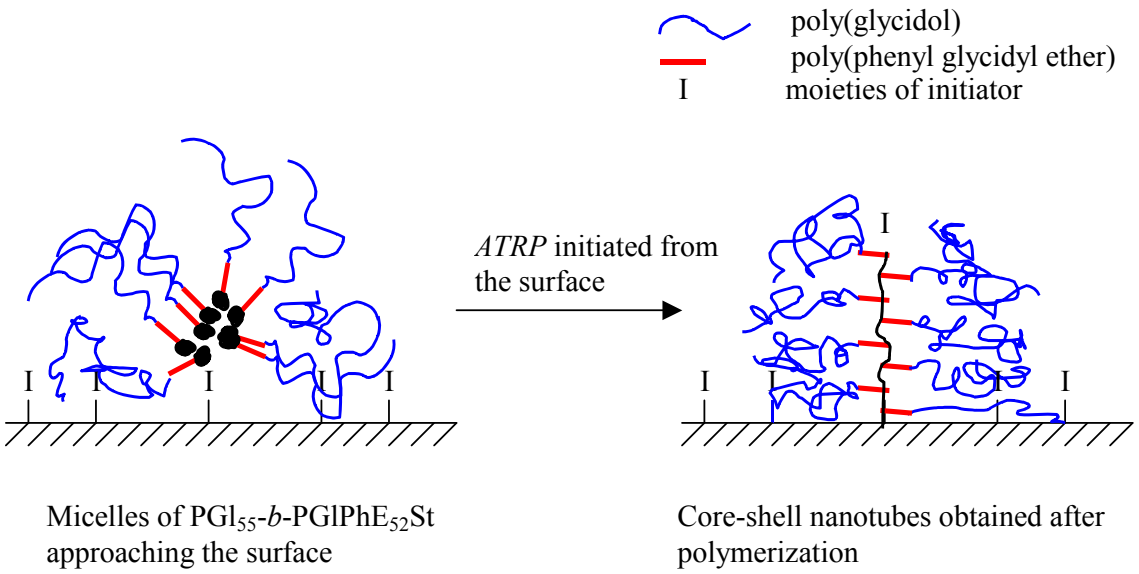


Figure 8.1. *ATRP* polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St initiated from the surface.

The idea seems to be interesting especially that the first experiments, however not confirmed, showed that *ATRP* initiator attached to the surface initiate the polymerisation of PGl_{52}-*b*-$PGlPhE_8$-St to give 8 nm thick films.

The obtained temperature sensitive polymacromonomers show reversible change of the properties from hydrophilic to hydrophobic upon change of the temperature and above T_c are insoluble in water. Thus, they could be used for example as *nano*-reactors with attached enzymes or other reactive moieties. At temperature under T_c, substances could diffuse into the particle and react influenced by attached to the polymacromonomer enzymes. However, if the undesired increase of the temperature occurred in the system the reaction would be stopped as the polymacromonomer with catalyst or enzymes would precipitate from the solution. It could prevent for example synthesis of side-products at higher temperatures.

Additionally, as the obtained polymacromonomers showed adsorption from the DMSO solutions the possible application could be as surface active polymeric additives for the surface modification of polymeric materials, what is very important in such field as biomaterials, chromatography, coating, adhesives, or antistatic properties.

9. Abbreviations list

AFM – Atomic Force Microscopy

AIBN – 2,2'-Azobis(isobutyronitrile*)*

ATRP – Atom Transfer Radical Polymerisation

AVA – *4,4'*-Azobis (*4*-cyanovaleric acid)

CMT – Critical micellization temperature

CMC – Critical micellization concentration

CPC – *α*-Chloropropionate chloride

CRP – Controlled Radical Polymerisations

DF – Degree of functionalisation

DHB – *2,5*-Dihydroxybenzoic acid

DLS – Dynamic Light Scattering

DMF – *N,N'*-Dimethylformamide

DMSO – Dimethyl sulphoxide

dn/dc – Refractive index increment

DP – Degree of polymerisation

DPH – *1,6*-Diphenyl-*1,3,5*-hexatriene

DSC – Differential Scanning Calorimetry

g – Shrinking factor

GC – Gas Chromatography

GlAc – Glycidol acetal

GlPhE – Phenyl glycidyl ether

GTP – Group Transfer Polymerisation

IR – Infrared Spectroscopy

k_d – Dissociation constant

k_p	– Propagation constant
k_t	– Termination constant
LCST	– Lowest Critical Solution Temperature
MALDI-TOF-MS	– Matrix-Assisted Laser Desorption Ionisation Time Of Flight Mass Spectroscopy
Me_6TREN	– Tris-(*2*-dimethylaminoethyl)amine
M_n	– Number average molecular weight
M_w	– Weight average molecular weight
M_w/M_n	–Dispersity index
NMR	– Nuclear Magnetic Resonance Spectroscopy
NMRP	– Nitroxy Mediated Radical Polymerisation
PEO	– Poly(ethylene oxide)
PEO_{2000}-Br	– *α*-Methoxy-*ω*-bromopropionate poly(ethylene oxide)
PGl	– Poly(glycidol)
PGl-St	– *α-t*–Butoxy-*ω*-vinylbenzyl-poly(glycidol)
PGlAc-St	– *α-t*–Butoxy-*ω*-vinylbenzyl-poly(glycidol acetal)
PGl-*b*-PGlPhE-St	– *α-t*–Butoxy-*ω*-vinylbenzyl- poly(glycidol)-*b*-poly(phenyl glycidyl ether)
PGlAc-*b*-PGlPhE-St	– *α-t*–Butoxy-ω-vinylbenzyl- poly(glycidol acetal)-*b*-poly(phenyl glycidyl ether)
PGlPhE-*b*-PGlAc-St	– *α-t*-Butoxy-*ω*-vinylbenzyl-poly(phenyl glycidyl ether)-*b*-poly(glycidol acetal)
PGlPhE-*b*-PGl-St	– *α-t*-Butoxy-*ω*-vinylbenzyl-poly(phenyl glycidyl ether)-*b*-poly(glycidol)
PS	– Poly(styrene)
RAFT	– Reversible Addition-Fragmentation Transfer

R_g	– Radius of gyration
R_h	– Hydrodynamic radius
R_p	– Rate of polymerisation
SEC	– Size Exclusion Chromatography
SEC-LALLS	– Size Exclusion Chromatography with Lowangle Laser Light Scattering Detector
SEC-MALLS	– Size Exclusion Chromatography with Multiangle Laser Light Scattering Detector
SFRP	– Stable Free Radical Polymerisation
SLS	– Static Light Scattering
SPM	– Scanning Probe Microscopy
tBuOK	– Potassium t-butoxide
T_c	– Cloud point
TEA	– Triethylamine
TFA	– Trifluoroacetic acid
T_g	– Glass transition temperature
THF	– Tetrahydrofuran
UV	– Ultraviolet
UV-VIS	– Ultraviolet-Visible Light Spectroscopy

10. References

1. K. Terao, Y. Nakamura, T. Norisue, *Macromolecules*, **1999**, *32*, 711.
2. K. Terao, T. Hakajo, Y. Nakamura, T. Norisue, *Macromolecules*, **1999**, *32*, 3690.
3. D. Sek, B. Kaczmarczyk, *Polymer* **1997**, *38*, 2925.
4. M. Zhang, T. Breiner, H. Mori, A. Müller, *Polymer*, **2003**, *44*, 1499.
5. S. Rathgeber, T. Pakula, A. Wilk, K. Matyjaszewski, K. Beers, *J. Chem. Phys*., **2005**, *122*, 124904.
6. M. Schappacher, C. Billaud, A. Paulo, A. Deffieux, *Macromol. Chem. Phys.*, **1999**, *200*, 2377.
7. A. Deffieux, M. Schappacher, *Macromolecules*, **1999**, *32*, 1797.
8. SW. Ryu, A. Hirao, *Macromolecules*, **2000**, *33*, 4765.
9. KL. Beers, SG. Gaynor, K. Matyjaszewski, SS. Sheiko, M. Möller, *Macromolecules*, **1998**, *31*, 9413.
10. HG. Börner, K. Beers, K. Matyjaszewski, SS. Sheiko, M. Möller, *Macromolecules*, **2001**, *34*, 4375.
11. G. Cheng, A. Böker, M. Zhang, G. Krausch, A. Müller, *Macromolecules*, **2001**, *34*, 6883.
12. W. Walach, A. Kowalczuk, B. Trzebicka, A. Dworak, *Macromol. Rapid Commun*., **2001**, *22*, 1272.
13. M. Neiser, J. Okuda, M. Schmidt, *Macromolecules*, **2003**, *36*, 5437.
14. Y. Aggour, I. Tomita, T. Endo, *React. Funct. Polym.*, **1995**, *28*, 81.
15. S. Aoshima, K. Ebara, T. Higashimura, *Polym. Bull.*, **1985**, *14*, 425.
16. R. Shen, T. Senyo, Ch. Akiyama, Y. Atago, K. Ito, *Polymer*, **2003**, *44*, 3221.
17. Y. Shen, S. Zhu, F. Zeng, R. Pelton, *Macromolecules*, **2000**, *33*, 5399.
18. T. Kitayama, O. Nakamura, K. Hatada, *Polym. J.*, **1996**, *28*, 150.
19. K. Yamada, M. Miyazaki, K. Ohno, T. Fukuda, M. Minoda, *Macromolecules*, **1999**, *32*, 290.
20. Y. Tsukahara, p. 161 Chapter 5 of *„Macromolecular Design: Concept and practice"* edited by M. Mishra, New York : Polymer Frontiers International, **1994**, USA.
21. K. Ito, K. Tanaka, H. Tanaka, G. Imai, S. Kawaguchi, S. Itsuno, *Macromolecules*, **1991**, *24*, 2348.
22. D. Chao, S. Itsuno, K. Ito, *Polym. J*., **1991**, *23*, 1045.

23. S. Kawaguchi, A. Yekeda, J. Duhamel, M. Winnik, K. Ito, *J. Phys. Chem.*, **1994**, *98*, 7891.
24. K. Ito, K. Hashimura, S. Itsuno, E. Yamada, *Macromolecules*, **1991**, *24*, 3997.
25. A. Sunder , R. Hanselmann, H. Frey, R. Mülhaupt*, Macromolecules,* **1999,** *32*, 4240.
26. E. J. Vandenberg, *J. Polym. Sci., Polym. Chem. Ed.,* **1985,** *23*, 915.
27. A. Dworak, W. Wałach, B. Trzebicka, *Macromol. Chem. Phys.*, **1995**, *196*, 1963.
28. D. Taton, A. Le Borgne, M. Sepulchre, N. Spassky, *Macromol. Chem. Phy*s., **1994,** *195*, 139.
29. A. Dworak, I. Panchev, B. Trzebicka, W. Wałach, *Macromol. Symp*., **2000**, *153*, 233.
30. W. Wałach, A. Kowalczuk, B. Trzebicka, A. Dworak, *Macromol. Rapid Commun.,* **2001**, *22*, 1272.
31. A. Dworak, G. Baran, B. Trzebicka, W. Wałach, *React. Funct. Polym.*, **1999**, *42*, 31.
32. A. Dworak, I. Panchev, B. Trzebicka, W. Wałach, *Macromol. Polym. Bull.*, **1998**, *40,* 461.
33. R. Milkovich, *Polym. Prepr.*, **1980**, *21*, 40.
34. G. Schultz, R. Milkovich, *J. Appl. Polym. Sci.,* **1982**, *27*, 4773.
35. G. Schultz, R. Milkovich, *J. Polym. Sci. Chem. Ed.* **1984**, *22*, 1633.
36. Y. Tsukahara, p. 94 Chapter 4 of *„Chemistry and Industry of macromonomers"* edited by Y. Yamashita, Basel, Heidelberg, New York : Hüthig & Wepf, **1993**.
37. M. Maniruzzman, S. Kawaguchi, K. Ito, *Macromolecules*, **2000**, *33*, 1583.
38. A. Hirao, S. Nakahama, *Prog. Polym. Sci*., **1992**, *17*, 283.
39. M. Sawamoto, *Prog. Polym. Sci*., **1991**, *16*, 111.
40. M. Brookhart, J. DeSimone, B. Grant, M. Tanner, *Macromolecules*, **1995**, *28*, 5378.
41. C. Hawker, J. Hedrick, *Macromolecules*, **1995**, *28*, 2993.
42. J. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.*, **1995**, *117*, 5614.
43. D. Mardare, K. Matyjaszewski, *Macromolecules*, **1994**, *27*, 645.
44. Y. Chujo, p. 36, Chapter 2 of *„Chemistry and Industry of macromonomers"* edited by Y. Yamashita, Basel, Heidelberg, New York : Hüthig & Wepf, **1993**.
45. S. Kobayashi, p. 1, Chapter 1 of *„Macromolecular Design: Concept and practice"* edited by M. Mishra, New York : Polymer Frontiers International, **1994**, USA.
46. K. Ishizu, p. 39, Chapter 2 of *„Macromolecular Design: Concept and practice"* edited by M. Mishra, New York : Polymer Frontiers International, **1994**, USA.
47. K. Ito, *Prog. Polym. Sci*., **1998**, *23*, 581.
48. K. Tsubaki, K. Ishizu, *Polymer*, **2001**, *42*, 8387.

49. S. Itsumo, D. Chao, K. Ito, J., *Polym. Sci.: Part A: Polym. Chem*., **1993**, *31*, 287.
50. K. Tsubaki, K. Ishizu, *Polymer*, **2001**, *42*, 8387. R. Asami, M. Takaki, H. Hanahata, *Macromolecules*, **1983**, *16*, 628.
51. B. Anderson, G. Andrews, P. Arthur, H. Jacobson, L. Melby, A. Playtis, W. Sharkey, *Macromolecules*, **1981**, *14*, 1599.
52. K. Ito, H. Tsuchida, A. Hayashi, T. Kitano, E. Yamada, T. Matsumo, *Polym. J*., **1985**, *17*, 827.
53. R. Asami, M. Takaki, Y. Moriyama, *Polym. Bull.*, **1986**, *16*, 125.
54. P. Rao, P. Masson, P. Lutz, G. Beinert, P. Rempp, *Polym. Bull*., **1984**, *11*, 115.
55. F. Sevarini, M. Pegoraro, L. Saija, *Angew. Makromol. Chem.*, **1985**, *133*, 111.
56. P. Lutz, P. Masson, G. Beinert, P. Rempp, *Polym. Bull.,* **1984**, *12*, 79.
57. M. Kubo; T. Hayashi, H. Kobayashi, T. Itoh, *Macromolecules*, **1998**, *31*, 1053.
58. M. Kubo, H. Takeuchi, T. Ohara, R. Nagahata, *J. Polym. Sci. Part A: Polym. Chem.,* **1999**, *37*, 2027.
59. Ph. Dubois, R. Jerome, Ph. Teyssie, *Macromolecules*, **1991**, *24*, 977.
60. Y. Kawakami, Y. Miki, T. Tsuda, R. Murthy, Y. Yamashita, *Macromol. Chem.,* **1984**, *185*, 9.
61. K. Hatada, H. Nakanishi, K. Ute, T. Kitayama, *Polym. J.*, **1986**, *18*, 581.
62. O. Webster, W. Hertler, D. Sogah, W. Farnham, T. Rayan Babu, *J. Am. Chem. Soc.,* **1983**, *105*, 5706.
63. W. Hertler, D. Sogah, O. Webster, B. Trost, Macromolecules, **1984**, *17*, 1415.
64. R. Asami, Y. Kondo, M. Takaki, *ACS Polym. Prepr.,* **1986**, *27 (1),* 186.
65. D. Sogah, O. Webster, *J. Polym. Sci., Polym. Lett. Ed.,* **1983**, *21*, 927.
66. T. Aida, S. Inoue, Macromolecules, **1981**, *14*, 1162.
67. T. Yasuda, T. Aida, S. Inoue, *Makromol. Rapid Commun.,* **1982**, *3*, 585.
68. T. Yasuda, T. Aida, S. Inoue, *J. Macromol. Sci.-Chem.,* **1984**, *A21*, 1035.
69. R. Asami, M. Takaki, K. Kita, E. Asakura, *Polym. Bull.,* **1984**, *11*, 121.
70. R. Asami, M. Takaki, K. Kyuda, E. Asakura, *Polym. J.,* **1984**, *15*, 139.
71. J. Sierra-Vargas, P. Masson, G. Beindert, P. Rempp, E. Franta, *Polym. Bull.,* **1982**, *7*, 277.
72. E. Goethals, M. Velgels, *Polym. Bull.,* **1981**, *4*, 521.
73. M. Takaki, R. Asami, T. Kuwabara, *Polym. Bull.,* **1982**, *7*, 521.
74. S. Kabayashi, M. Kaku, S. Sawada, T. Saegusa, *Polym. Bull.,* **1985**, *13*, 447.
75. M. Miyamoto, K. Naka, M. Tokumizu, T. Saegusa, *Macromolecules*, **1989**, *22*, 1604.

76. J. Sierra-Vegas, J. Zilliox, P. Rempp, E. Franta, *Polym. Bull.,* **1980**, *3*, 83
77. E. Burgess, A. Cunliffe, D. Richards, D. Thompson, *Polymer*, **1978**, *19*, 334.
78. S. Yu, *ACS Polym. Prep.,* **1986**, *27 (2)*, 234.
79. J. Kennedy, *Polym. J.*, **1980**, *12*, 609.
80. S. Aoshima, K. Ebata, T. Higashimura, *Polym. Bull.,* **1985**, *14*, 425.
81. K. Ito, N. Usami, Y. Yamashita, *Macromolecules*, **1980**, *13*, 216.
82. Y. Yamashita, T. Tsukahara, K. Ito, K. Okada, Y. Tajima, *Polym. Bull*., **1981**, *5*, 335.
83. Y. Chujo, T. Shishino, Y. Tsukahara, Y. Yamashita, *Polym. J.*, **1985**, *17*, 133.
84. M. Niwa, T. Hayashi, T. Matsumoto, *J. Makromol. Sci. Chem.*, **1986**, *A23*, 433.
85. M. Niwa, T. Hayashi, M. Akahori, *J. Makromol. Sci. Chem.*, **1987**, *A24*, 49.
86. Y. Yamashita, K. Ito, H. Mizuno, K. Okada, *Polym. J*., **1982**, *14*, 255.
87. M. Akashi, I. Kirikihara, N. Miyaushi, *Angew. Makromol. Chem*., **1983**, *132*, 81.
88. B. Boutevin, Y. Pietrasanta, H. Taha, T. Sarraf, *Polym. Bull.*, **1983**, *10*, 157.
89. G. Meijs, E. Rizzardo, S. Thang, *Macromolecules*, **1988**, *21*, 3122.
90. K. Matyjaszewski, K. Beers, A. Kern, S. Gaynor, *J. Polym. Sci. Part A: Polym. Chem.***,** **1998**, *36*, 823.
91. Y. Nakagawa, K. Matyjaszewski, *Polym. J.*, **1998**, *30*, 138.
92. M. Maeda, Y. Nitadori, T. Tsuruta, *Makromol. Chem.,* **1980**, *181*, 2245.
93. T. Nishimura, M. Maeda, Y. Nitadori, T. Tsuruta, *Makromol. Chem.,* **1982**, *183*, 29.
94. P. Ferruti, E. Ranucci, *Polym. J.,* **1991**, *23*, 541.
95. S. Kabayashi, E. Masuda, S. Shoda, Y. Shimano, *Macromolecules*, **1989**, *22*, 2878.
96. T. Kitayama, S. Kishiro, K. Hatada, *Polym. Bull.*, **1991**, *24*, 2151.
97. S. Hudecek, J. Spevacek, J. Hudeckowa, J. Mikesova, *Polym. Bull.*, **1980**, *3*, 143.
98. K. Ito, S. Yokoyama, F. Arakawa, Y. Yukawa, T. Iwashita, Y. Yamashaki, *Polym. Bull.*, **1986**, *16*, 337.
99. K. Ito, S. Yokoyama, F. Arakawa, *Polym. Bull.*, **1986**, *16*, 345.
100. Y. Kawakami, Y. Miki, T. Tsuda, R. Murthy, Y. Yamashita, *Macromol. Chem.,* **1982**, *14*, 913
101. J. Liu, C. Chew, L. Gan, *J. M. S-Pure Appl. Chem.*, **1996**, *A 33 (3)*, 337.
102. P. Masson, G. Beinerd, E. Franta, P. Rempp*., Polym. Bull.,* **1982**, *7*, 17.
103. S. Kobayashi, T. Mizutani, T. Saegusa, *Makromol. Chem.,* **1984**, *185*, 441.
104. E. Nomura, K. Ito, A. Kajiwara, M. Kamachi, *Macromolecules*, **1997**, *30*, 2811.
105. K. Ito, Y. Tomi, S. Kawaguchi, *Macromolecules*, **1992**, *25*, 1534.

106. R. Morrison, R. Boyd, *Organic Chemistry*, Third Edition, Allyn and Bacon, Inc. Boston, **1997**.
107. T. Basinska, S. Slomkowski, A. Dworak, I. Panchev, M. Chehimi, *Colloid Polym. Sci*., **2001**, *279*, 916.
108. J. Kennedy, M. Hiza, *J. Polym. Sci. Polym. Chem. Ed.,* **1983**, *21*, 1033.
109. R. Velichkova, D. Christova, *Prog. Polym. Sci.,* **1995**, *20*, 819.
110. K. Ishizu, S. Uchida, *Prog. Polym. Sci.*, **1999**, *24*, 1439.
111. D. Knauss, T. Huang, *Macromolecules,* **2003**, *36*, 6036.
112. K. Ito, S. Kawaguchi, *Advan. Polym. Sci*. **1999**, *142*, 129.
113. Y. Tsukahara, K. Mizuno, A. Segawa, Y. Yamashita, *Macromolecules,* **1989**, *22*, 1546.
114. Y. Tsukahara, K. Mizuno, A. Segawa, Y. Yamashita, *Macromolecules,* **1989**, *22*, 2869.
115. Y. Tsukahara, K. Tsutsumi, Y. Yamashita, S. Shimada, *Macromolecules,* **1990**, *23*, 5201.
116. K. Tsutsumi, Y. Okamoto, Y. Tsukahara, *Polymer*, **1994**, *35*, 2205.
117. F. Bovey, F. Winslov, "Macromolecules; an introduction to polymer science", New York, London, Academic Press, **1979**.
118. P. Rempp, P. Lutz, P. Masson, P. Chaumont, E. Franta, *Makromol. Chem.., Suppl.* **1985**, *13*, 47.
119. P. Masson, E. Franta, P. Rempp, *Makromol. Chem.. Rapid. Commun,* **1982**, *3*, 499.
120. K. Hatada, T. Shinozaki, K. Ute, T. Kitayama, *Polym. Bull.,* **1988**, *19*, 231.
121. G. Russell, D. Napper, R. Gilbert, *Macromolecules,* **1988**, *21*, 2133.
122. T. Hamaide, A. Revillon, A. Guyot, *Eur. Polym. J.*, **1984**, *20*, 855.
123. T. Stephan, S. Muth, M. Schmidt, *Macromolecules*, **2002**, *35*, 9857.
124. G. Riess, *Prog. Polym. Sci*., **2003**, *28*, 1107.
125. K. Prochazka, T. Martin, S. Webber, P. Munk, *Macromolecules*, **1996**, *29*, 6526.
126. R. Xu, M. Winnik, F. Hallett, G. Riess, M. Croucher, *Macromolecules*, **1991**, *24*, 87.
127. G. Zhu, *Eur. Polym. J*, **2005**, *41*, 2671.
128. L. Bronstein, D. Chernyshov, G. Timofeeva, L. Dubrovina, P. Vatelsky, *Langmuir*, **1999**, *15*, 6195.
129. I. Capek, M. Akashi, *JMS Rev. Macromol. Chem. Phys.*, **1993**, *C33*, 369.
130. I. Capek, *Advan. Colloid Interface Sci,* **2000**, *88*, 295.
131. K. Liu, J. Parsons, *Macromolecules*, **1969**, *1*, 529.
132. P. Ferguson, D. Sherrington, A. Gough, *Polymer*, **1993**, *34*, 3281.

133. S. Maiti, P. Chtterji, C. Nisha, S. Manorama, V. Aswal, P. Goyal, *J. Colloid Interface Sci.*, **2001**, *240*, 630.
134. S. Maiti, P. Chtterji, *J. Colloid Interface Sci.*, **2000**, *232*, 273.
135. E. Nomura, K. Ito, *Macromolecules*, **1997**, *30*, 2811.
136. E. Nomura, K. Ito, A. Kajiwara, M. Kamachi, *Polym. Bull.*, **1989**, *22*, 123.
137. H. Furuhashi, S. Kawaguchi, S. Itsuno, K. Ito, *Macromolecules.,* **1997**, *30*, 2811.
138. I. Capek, *Advan. Polym. Sci*. **1999**, *145*, 1.
139. K. Ito, H. Kobayashi, *Polym. J*., **1992**, *24*, 199.
140. Y. Kim, O. Webster, *J. Am. Chem. Soc.*, **1990**, *112*, 4592.
141. B. Voit, S. Turner „The polymeric materials encyclopedia: synthesis, properties and applications“ CRC Press, Boca Raton Florida, USA, p. 3177, **1996.**
142. E. Malstrom, A. Hult, U. Gedde, F. Liu, R. Boyd, *Polymer*, **1997**, *38*, 4873.
143. T. Fox, P. Flory, *J. Appl. Phys.*, **1950**, *21*, 581.
144. Y. Tsukahara, K. Tsutsumi, Y. Okamoto, *Macromol. Rapid Commun.,* **1992**, *13*, 409.
145. Y. Tsukahara, J. Inoue, Y. Ohata, S. Kojiya, *Polymer*, **1994**, *35*, 5785.
146. S. Sheiko, M. Gerle, K. Fisher, M. Schmidt, M. Möller, *Langmuir*, **1997**, *13*, 5368.
147. Y. Tsukahara, Y. Ohta, K. Senoo, *Polymer*, **1995**, *36*, 3413.
148. Y. Tsukahara, *Macromolecular Reports*, **1995**, *A32*, 821.
149. Y. Kim, O. Webster, *Macromolecules*, **1992**, *25,* 5561
150. L. Boogh, B. Petterson, J. Manson, *Polymer*, **1999**, *40*, 249
151. G. Bo, B. Wesslen, K. Wesslen, *J. Polym. Sci. Part A: Polym. Chem.,* **1992**, *30*, 1799.
152. G. Berry, *J. Polym. Sci. Part A2: Polym. Chem*., **1968**, *6*, 1551.
153. V. Heroguez, Y. Gnanou, M. Fontanille, *Macromol. Rapid. Commun.*, **1996**, *17*, 137.
154. V. Heroguez, B. Breuning, , Y. Gnanou, M. Fontanille, *Macromolecules.,* **1996**, 29, 4459.
155. V. Heroguez, Y. Gnanou, M. Fontanille, *Macromolecules*, **1997**, *30*, 4791.
156. S. Kawaguchi, K. Akaike, Z. Zhang, H. Matsumoto, K. Ito, *Polym. J.,* **1998**, *30*, 1004
157. S. Kawaguchi, G. Imai, J. Suzuki, A. Miyahara, T. Kitano, K. Ito, *Polymer*, **1997**, *38*, 885.
158. B. Brenning, V. Heroguez, Y. Gnanou, M. Fontanille, *Macromol. Symp.,* **1995**, *95*, 151
159. Y. Tsukahara, S. Kohjiya, K. Tsutsumi, Y. Okamoto, *Macromolecules*, **1994**, *27*, 1662.
160. K. Terao, Y. Nakamura, T. Norisuye, *Macromolecules*, **1999**, *32*, 711.
161. K. Terao, T. Hokajo, Y. Nakamura, T. Norisuye, *Macromolecules*, **1999**, *32*, 3690.
162. K. Tsubaki, H. Kobayashi, J. Sato, K. Ishizu, *J. Colloid Interface Sci.*, **2001**, *241*, 275.

163. K. Ishizu, K. Tsubaki, T. Ono, *Polymer*, **1998**, *39*, 2935.
164. K. Tsubaki, K. Ishizu, *Polymer*, **2001**, *42*, 8387.
165. M. Wintermantel, M. Schmidt, Y. Tsukahara, K. Kajiwara, S. Kohjiya, *Macromol. Rapid. Commun.*, **1994**, *15*, 279.
166. M. Wintermantel, M. Gerle, K. Fisher, M. Schmidt, I. Wataoka, K. Kajiwara, Y. Tsukahara, *Macromolecules*, **1996**, *29*, 978.
167. H. Kawaguchi, *Prog. Polym. Sci.*, **2000**, *25*, 1171.
168. C. Durrer, J. Irache, D. Duchende, G. Ponchel, *J. Colloid Interface Sci.*, **1995**, *170*, 555.
169. B. Vincent, J. Edwards, S. Emmett, A. Jones, *A. Colloids Surf.*, **1986**, *18*, 261.
170. C. Ober, K. Lok, *Macromolecules,* **1987**, *20*, 268.
171. S. Kawaguchi, M. Winnik, K. Ito, *Macromolecules*, **1995**, *28*, 1159.
172. H. Uyama, Y. Matsumoto, S. Kobayashi, *Chem. Lett*., **1992**, 2401.
173. Y. Tsukahara, p. 297 Chapter 4 of *„Chemistry and Industry of macromonomers"* edited by Y. Yamashita, Basel, Heidelberg, New York : Hüthig & Wepf, **1993**.
174. Y. Shibata, S. Kawaguchi, K. Ito, *Polym. Prepr. Japan*, **1992**, *41*, 28.
175. J. Lukaszczyk, A. Cebulska, *Polimery*, **2000**, *45*, 674.
176. I. Capek, M. Riza, M. Akashi, *Polym. J.*, **1992**, *24*, 959.
177. S. Kobayashi, T. Mizutani, T. Segusa, *Macromol. Chem*., **1984**, *185*, 441.
178. Z. Mitov, R. Velichkova, T. Zlatkov, *Eur. Polym. J.*, **1990**, *29*, 1129.
179. E. Rietman, M. Kaplan, *J. Polym. Sci. Part C. Polym. Lett.,* **1990**, *28*, 187.
180. S. Zhang, G. Liu, L. Yang, *J. Polym. Sci. Part A, Polym. Chem.*, **1993**, *31*, 2313.
181. G. Zhou, I. Khan, Y. Smid, *Polym. Commun.*, **1989**, *30*, 52.
182. P. Gramain, Y. Frere, *Polym. Commun*., **1986**, *27*, 16.
183. K. Kim, S. Cho, Y. Kim, *Polym. J.,* **1993**, *26*, 4083.
184. C. Song, H. Sun, X. Feng, *Polym. J.,* 1987, *19*, 485.
185. F. Snardi, A. Zubir, Y. Sabarinach, W. Sofitarti, *J. Macromol. Sci. Chem.*, **1987**, *A24*, 1369.
186. H. Harwood, *Encyclopaedia of Polymer Science and Engineering*, 2nd edn, ed. J. Kroschwitz, Willey Interscience, New York, **1989**, Suppl. Vol., *708-867.*
187. M. Szwarc , M. Van Beylen „*Ionic polymerisation and Living Polymers*" Chapman and Hall, N. York, London **1993**.
188. M. Szwarc „*Ionic polymerisation fundamentals*" Hansen Publishers, New York **1996**.
189. M. Szwarc, *Adv. Polym. Sci.* **1983**, *49*, 1.

190. H. Hsieh, R. Ouirk „ *Anionic polymerisation: Principles and Application*" Marcel Dekker, New York, Bazylea, Hong-Kong **1996.**
191. K. Matyjaszewski, J.Xia, *Chem.Rev.*, **2001**, *101*, 2921.
192. K. Davis, K. Matyjaszewski, *Macromolecules* **2000**, *33*, 4039.
193. C. Hawker, J. Fréchet, R. Grubbs, J. Dao, *J. Am. Chem. Soc*., **1995,** *117*, 10763.
194. J. Chiefari, Y. Chong, F. Ercole, J. Krstina, J. Jeffery, R. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. Thang, *Macromolecules*, **1998**, *31*, 5559.
195. D. Colombani, *Prog. Polym. Sci*., **1997**, *22*, 1649.
196. H. Dostal, H. Mark, *Z. Phys. Chem. B.*, **1953**, *29*, 299.
197. M. Szwarc, *Nature*, **1956**, *178*, 1168.
198. A. Duda, *Polimery*, **1998**, *43*, 135.
199. S. Boileau, „*Anionic Ring-Opening Polymerisation: Epoxides and Episulfides*, pp. 467-487 in "*Comprehensive Polymer Science*" ed. Pergamon Press, London, **1989**
200. S. Baywater, *Prog. Polym. Sci*, **1975**, *4*, 27.
201. P. Munk "*Introduction to Macromolecular Science*" A Wiley-Interscience Publication, New York, Chichester, Brisbane, Toronto, Singapore **1989.**
202. G. Gee, W. Higginson, G. Merall, *J. Chem. Soc*., **1959**, 1345.
203. G. Gee, W. Higginson, P. Levesley, K. Taylor, *J. Chem. Soc*., **1959**, 1338.
204. J. Figuereulo, D. Worsfold *Eur. Polym. J*., **1968**, *4*, 439.
205. L. Blanchard, *J.Polym.Sci., Part A*, **1972**, *10*, 3082.
206. J. Figuereulo, S. Nenna, *Makromol.Chem.,* **1975**, *176*, 3377.
207. J. Figuereulo, M. Rodrigez, *Makromol.Chem.,* **1975**, *176*, 3107.
208. A. Deffieux, S. Boileau, *Polymer*, **1977**, *18*, 1047.
209. C. Einsbach, M. Pauscher, *Makromol.Chem.Rapid Commun.* **1980**, *1*, 105.
210. E. Vandenberg, *J. Polym. Sci., Polym. Chem. Ed.,* **1985,** *23*, 915.
211. D. Taton, A. Le Borgne, M. Sepulchre, N. Spassky, *Macromol. Chem. Phy*s., **1994,** *195*, 139.
212. S. Sandler, F. Berg, J. Polym. Sci. Part A-1, **4**, 1253 (1966).
213. R. Tokar , P. Kubisa , S. Penczek , A. Dworak *Macromolecules* **1994,** *27*, 320.
214. A. Sunder , R. Hanselmann, H. Frey, R. Mülhaupt*, Macromolecules* **1999,** *32*, 4240.
215. A. Kleman, R. Wagner " *Glycidol, Properties, Reactions, Applications*" Hüting, Heidelberg, Basel, New York, **1980**.
216. A. Fitton, J. Hill, D. Jane, R. Miller, *Synthesis,* **1987,** 1140.

217. H. Harwood, Encyclopaedia of Polymer Science and Engineering, 2nd edn, ed. J. Kroschwitz, Willey Interscience, New York, 1989, Suppl., Vol., 429-437.
218. K. Matyjaszewski, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1995**, *36 (1)*, 541.
219. G. Odian, *Principles of polymerisation,* 3rd edn. Willey, New York, **1991**, pp. 280-281.
220. J. Xia, K. Matyjaszewski, *ACS Symp. Ser*., **2000**, *760*, 207.
221. W. Coessens, T. Pintauer, K. Matyjaszewski, *Prog. Polym. Sci*., **2001**, *26*, 337.
222. H. Nagashima, N. Ozaki, M. Ishii, K. Seki, M. Washiyama, K. Itoh *Org. Chem.* **1993**, *58*, 464.
223. M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev*., **2001**, *101*, 3689.
224. K. Matyjaszewski , T. Patten , J. Xia, *J. Am. Chem. Soc.* **1997**, *119*, 674.
225. K. Matyjaszewski, K. Davis, T. Patten, M. Wei, *Tetrahedron*, **1997**, *53*, 15321.
226. S. Pascaul, B. coutin, M. Tardi, A. Palton, J. Vairon, *Macromolecules*, **1999**, *32*, 1432.
227. X. Wang, S. Armes, Macromolecules, **2000**, *33*, 6640.
228. K. Matyjaszewski, K. Nakagawa, C. Jasieczek, *Macromolecules,* **1998**, *31*, 1535.
229. K. Matyjaszewski, S. Coca, S. Gaynor, S. Wei, B. Woodworth, *Macromolecules,* **1997**, *30*, 7348.
230. K. Matyjaszewski, S. Coca, S. Gaynor, S. Wei, B. Woodworth, *Macromolecules,* **1998**, *31*, 5967.
231. A. Kajiwara, K. Matyjaszewski, M. Kamachi, *Macromolecules*, **1998**, *31*, 5695.
232. jakas literatura o zelowce
233. F. Hellienkamp, M. Karas, R. Beavis, B. Chait, *Analytical Chemistry*, **1991**, *63*, 1193-1203.
234. B. Mamyrin, V. Karataev, D. Schmikk, V. Zagulin, *Sov. Phys*. JETP, **1973**, *37*, 45.
235. H. Katayama, H. Kitaguchi, M. Kamigaito, M. Sawamoto, *J. Polym. Sci. Part A: Polym. Chem.*, **2000**, *38*, 4023.
236. literature do afm
237. W. Burchard, W. Richtering, *Progr. Coll. Polym. Sci*., **1989**, *80*, 151.
238. W. Burchard, *Adv. Polym. Sci*., **1999**, *143*, 113.
239. A. Dworak, I. Panchev, B. Trzebicka, W. Walach, *Polym. Bull.*, **1998**, *40*, 461.
240. S. Liu, J. Weaver, Y. Tang, N. Bilingham, S. Armes, *Macromolecules*, **2002**, *35*, 6121.
241. A. Dworak, B. Trzebicka, A. Utrata, W. Walach, *Polym. Bull*., **2003**, *50*, 47.
242. P. Kratochvil, "*Classical Light Scattering from Polymer Solutions*" Elsevier, Amsterdam-Oxford-New York-Tokyo 1987.

243. P. Alexandridis, J. Holzwarth, T. Hatton, Macromolecules, **1994**, *27*, 2414.

244. A. Laschevsky, E. Rekai, E. Wischerhoff, *Macromol. Chem. Phys.*, **2001**, *202*, 276.

245. M. Husseman, E. Malmstörn, C. Hawker, *Macromolecules*, **1999**, *32*, 1424.

246. B. Zhao, W. Brittain, *Prog. Polym. Sci.,* **2000**, *25*, 677.

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Hiermit erkenne ich die Promotionsordnung der Fakultät Mathematik und Naturwissenschaften an der Technischen Universität Dresden vom 20. März 2000, in der Fassung der vom Fakultätsrat am 19.06.2002 und 12.07.2002 beschlossenen und mit Erlass des Sächsischen Staatsministeriums für Wissenschaft und Kunst vom 18.03.2003 genehmigten Änderungen gemäß Satzung vom 16.04.2003 an.

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